

# **A Highly Reduced Ni-Li-Olefin Complex for Catalytic Kumada-Corriu Cross-Couplings**

Lukas Nattmann, Sigrid Lutz, Pascal Ortsack, Richard Goddard and Josep Cornella\*

Max-Planck-Institut für Kohlenforschung, Kaiser-Wilhelm-Platz 1, Mülheim an der Ruhr, 45470, Germany.

[cornella@kofo.mpg.de](mailto:cornella@kofo.mpg.de)

## **Supporting Information**

# 1 Contents

2	General Experimental Notes.....	S3
3	Preparation of Complex <b>1</b> .....	S4
4	Stoichiometric Experiments.....	S8
5	Preparation of the Oxidative Addition Complex <b>21</b> .....	S9
6	Procedure for Scheme 2.....	S10
7	Kinetic Studies.....	S12
8	Procedures for Scheme 3 .....	S13
9	Homogeneity Tests .....	S14
10	Starting Material Preparation.....	S18
11	Kumada Cross-Coupling catalyzed by Complex <b>1</b> .....	S24
12	X-Ray characterization .....	S34
13	NMR Spectra .....	S44
14	References .....	S59

## 2 General Experimental Notes

Unless otherwise stated, all manipulations were performed using Schlenk techniques under dry argon in heatgun-dried glassware. Exceptionally rigorous technique was observed when handling complex **1** compounds. The respective Schlenk flasks housing the complexes were maintained at  $-78\text{ }^{\circ}\text{C}$  in a dewar filled with dry ice. Rapid decomposition is observed when complex **1** is subjected to elevated temperatures (rt and above). Measurements of precatalyst weight were undertaken as rapidly as possible to avoid unnecessary warming, and immediately returned to cool temperatures after recording the weight. Anhydrous solvents were distilled from appropriate drying agents and were transferred under Argon: THF, Et<sub>2</sub>O (Mg/anthracene), CH<sub>2</sub>Cl<sub>2</sub> (CaH<sub>2</sub>), CH<sub>3</sub>CN (CaH<sub>2</sub>), hexane, toluene (Na/K), EtOH, MeOH (Mg), Et<sub>3</sub>N (MS), DMF (MS), MTBE (CaH<sub>2</sub> + MS). Commercially available Grignard reagents were obtained from Sigma Aldrich. Flash chromatography: Merck silica gel 60 (40-63  $\mu\text{m}$ ). MS (EI): Finnigan MAT 8200 (70 eV), ESI-MS: ESQ 3000 (Bruker). Accurate mass determinations: Bruker APEX III FT-MS (7 T magnet) or MAT 95 (Finnigan). NMR spectra were recorded using a Bruker Avance III HD 400 MHz spectrometer. <sup>1</sup>H NMR spectra (400 MHz) were referenced to the residual protons of the deuterated solvent used. <sup>13</sup>C NMR spectra (101 MHz) were referenced internally to the D-coupled <sup>13</sup>C resonances of the NMR solvent. Chemical shifts ( $\delta$ ) are given in ppm, relative to deuterated solvent residual peak, and coupling constants (*J*) are provided in Hz. TEM and EPX were recorded on a TEM Hitachi HF2000 with 200 kV cold-FEG under argon.

### Graphical guide to the use of Ar trousers.

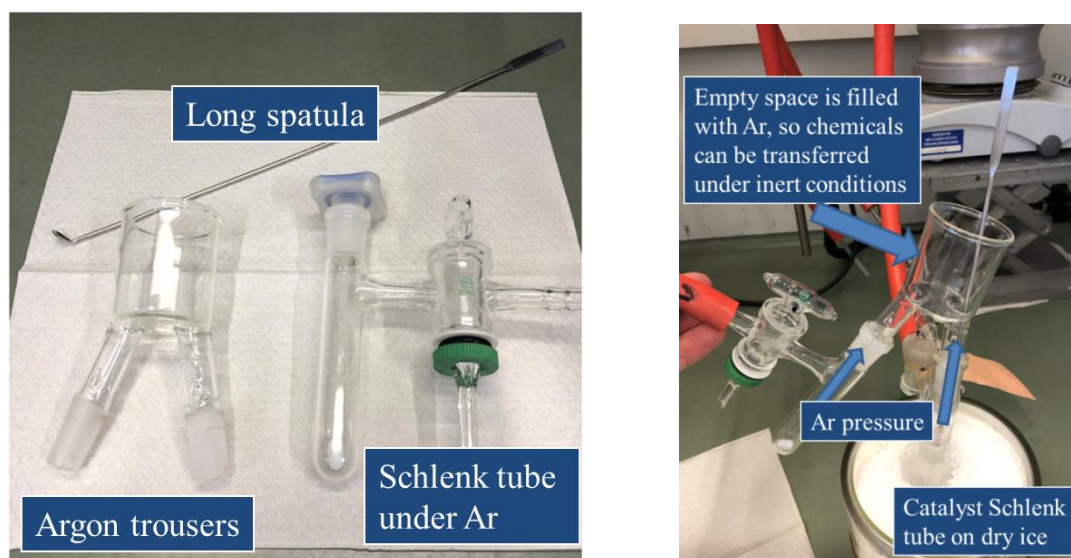
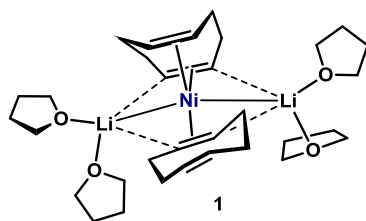


Figure S1

### 3 Preparation of Complex 1

A Schlenk tube was charged with Ni(COD)<sub>2</sub> (1.00 g, 3.63 mmol) *via* argon trousers and dissolved in freshly dried THF (10 mL). The solution was cooled to 0 °C and Li sand (90 mg, ~ 5 eq.) was added *via* argon trousers. The reaction was stirred at 0 °C for 3 hours and the solution adopted a deep orange hue.

Simultaneously a second Schlenk tube and a cooling frit (D4) equipped with an argon attachment were assembled. The cooling coat of the frit was cooled to 0 °C and the suspension from the first Schlenk was transferred quickly with a positive pressure of argon through an inert tube onto the frit, and filtered, with excess lithium remaining on the frit. The solution in the Schlenk was diluted with freshly dried and precooled Et<sub>2</sub>O (10 mL), further cooled to -78 °C, and maintained at that temperature overnight. The desired precatalyst was observed to spontaneously precipitate. Subsequently, the Schlenk was warmed to -30 °C and the mother liquor was transferred to a third Schlenk tube with argon pressure *via* a thin glass tube. The remaining solid was washed with precooled Et<sub>2</sub>O (5 mL) and the solution was again transferred to the third Schlenk tube, and sequentially repeated twice. The remaining purified precatalyst was then dried *in vacuo* (1 × 10<sup>-3</sup> mbar) for two hours at -30 °C. The obtained precatalyst (1.26 g, 2.03 mmol, 56 %) was stored under argon on dry ice and found to be storable under these conditions for several months.



<sup>1</sup>H NMR (-40 °C, 400 MHz, THF-*d*<sub>8</sub>) δ 5.53 (bs, 2H), 3.63 – 3.58 (m, 16H), 3.04 (bs, 2H), 2.21 – 1.95 (m, 14H), 1.80-1.73 (m, 16H), 1.19 (bs, 2H), 1.02 (bs, 2H), 0.73 (bs, 2H).

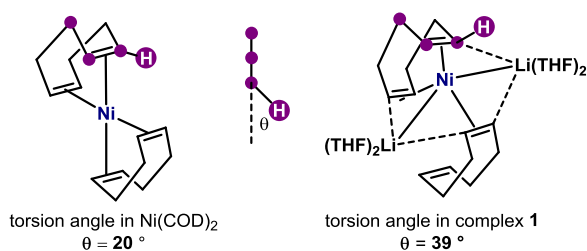
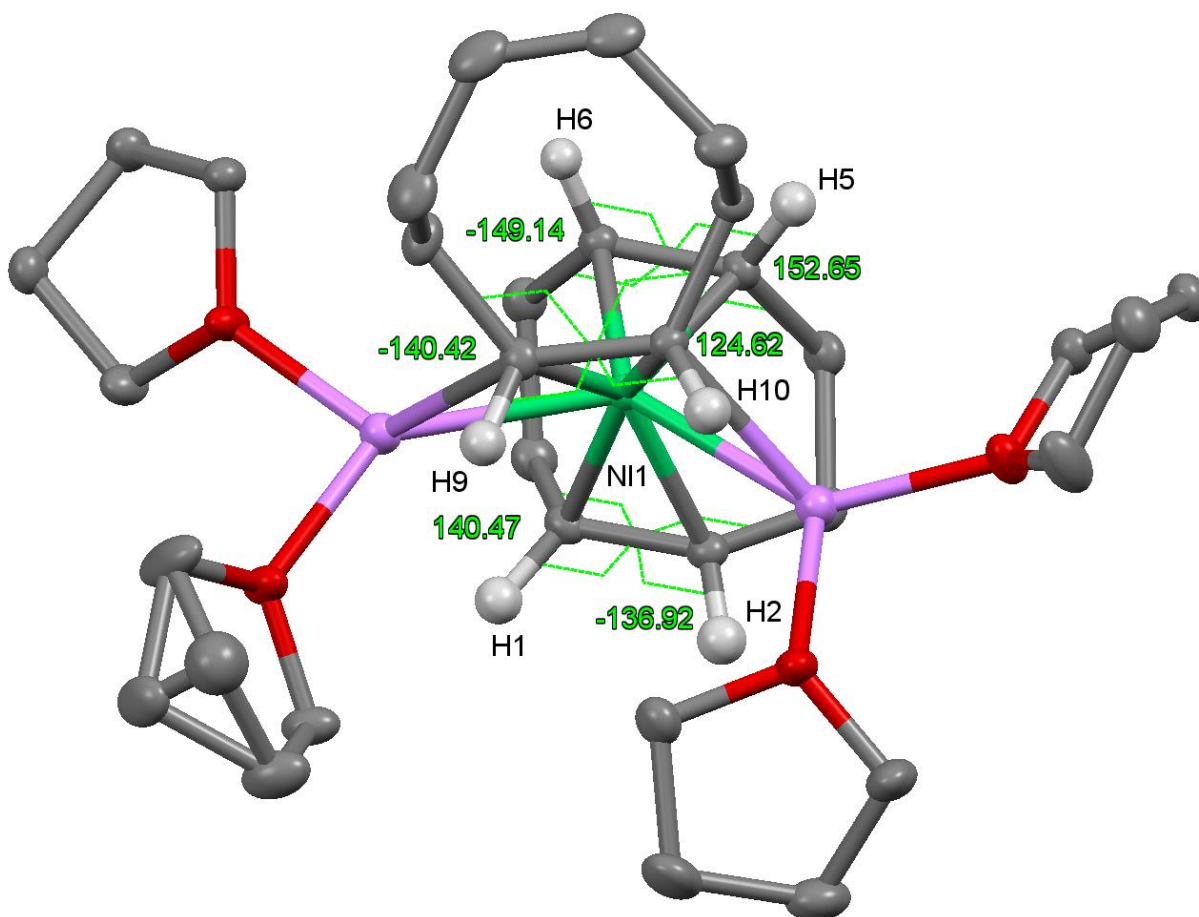
<sup>13</sup>C NMR (-40 °C, 101 MHz, THF-*d*<sub>8</sub>) δ 131.2 (bs), 67.3, 42.9 (bs), 38.0 (bs), 37.3 (bs), 35.9 (bs), 33.6(bs), 25.5.

<sup>7</sup>Li NMR (-40 °C, 156 MHz, THF-*d*<sub>8</sub>) δ 3.09 (s)

#### Structural Analysis Compound 1:

*Torsion angles:* The pyramidalization of the C(sp<sup>2</sup>) in the olefins is a common feature when utilizing 1,5-cyclooctadiene and other strained cyclic olefins with Ni. We have analyzed the torsion angles as shown in Scheme S1. We compared the angles from Ni(COD)<sub>2</sub><sup>1</sup> with complex **1** and found that a higher degree of

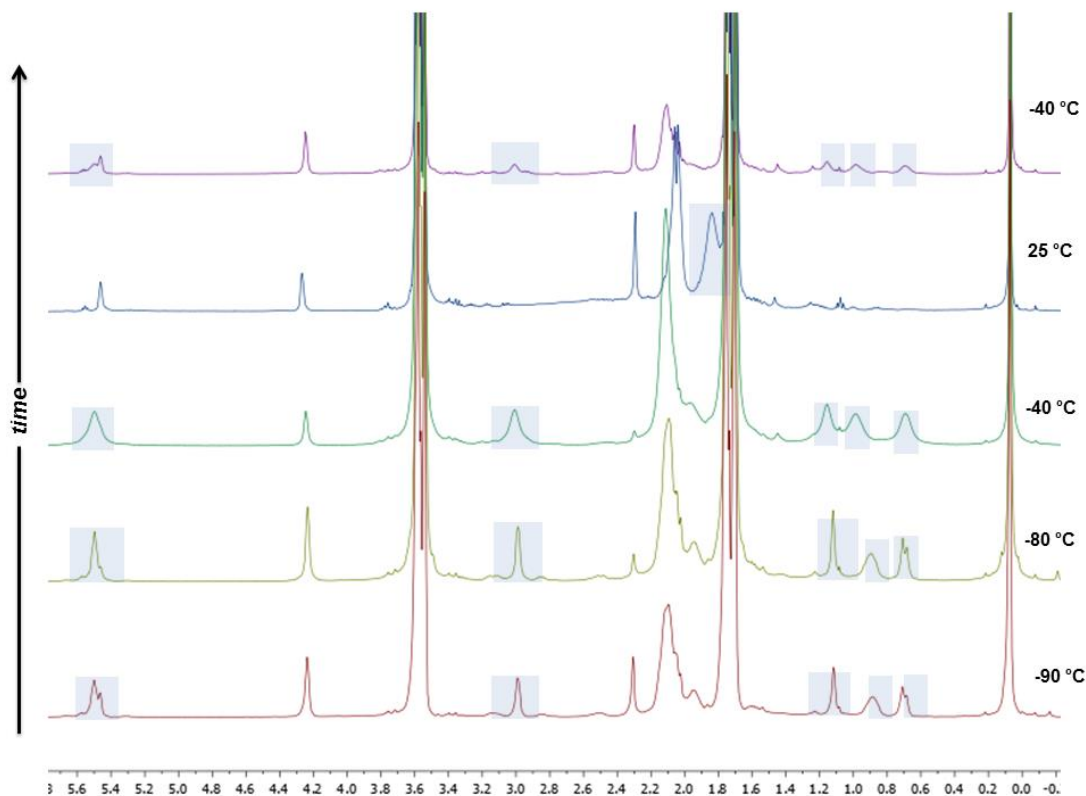
pyramidalization of the carbon atoms was observed for **1** (20° to 39° respectively). It is worth mentioning that the angle values are the result of averaging all the torsion angles in the crystal structure. This rehybridization of **1** is in accordance to the Dewar-Chatt-Duncanson model and is consistent with a large amount of charge being redistributed at the  $\pi$  system through  $\pi$ -back-donation.



**Scheme S1**

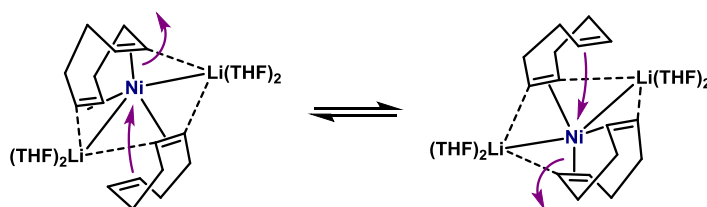
Although an increase in pyramidalization is observed in **1** when compared to  $\text{Ni}(\text{COD})_2$ , the  $\text{C}(\text{sp}^2)$  still retain a  $\text{sp}^2$  character and remain labile to exchange reactions as demonstrated by the dynamic fluxional behavior (*vide infra*).

Geometry of complex **1** in solution: As shown by the X-ray data, in the crystal structure complex **1** has a distorted trigonal bipyramidal geometry. However, variable temperature NMR studies revealed a fluxional behavior in solution (Scheme S2).



**Scheme S2**

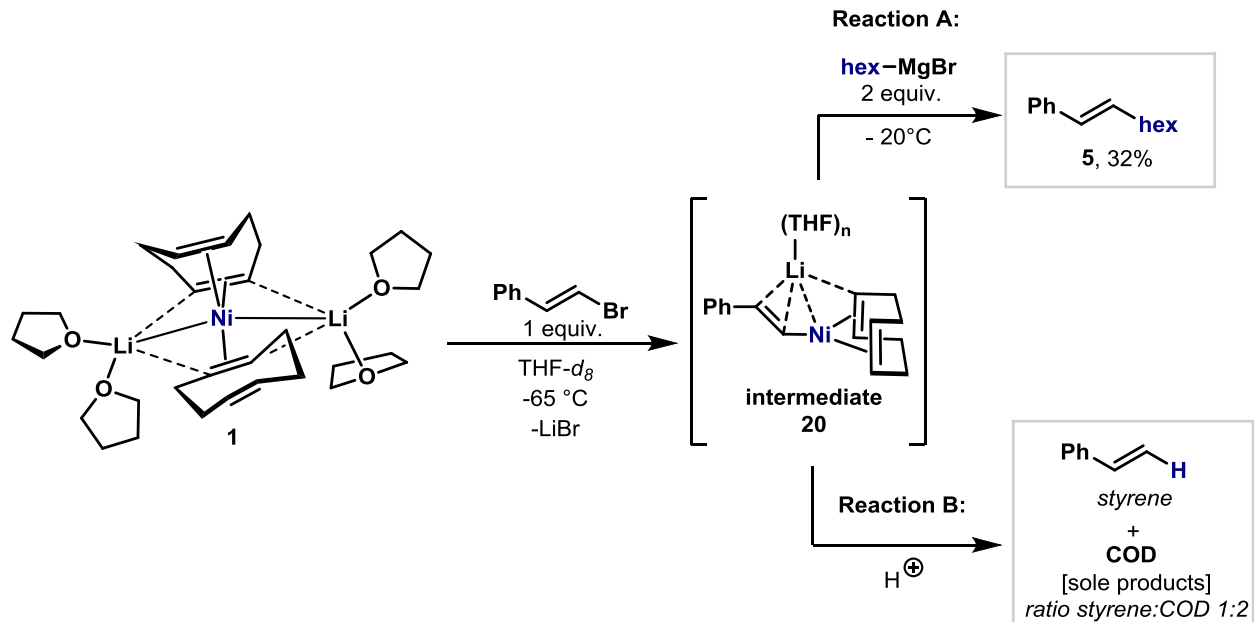
When the temperature is increased from  $-40\text{ }^{\circ}\text{C}$  to  $25\text{ }^{\circ}\text{C}$ , the signals for the olefins reach a coalescence point and appear as one broad signal at 1.84 ppm. Importantly, when the same sample is then cooled down beyond the coalescence point (back to  $-40\text{ }^{\circ}\text{C}$ ), the characteristic signals for **1** observed at low temperature appear again. These results are in agreement with those reported by Jonas *et al.* (*Angew. Chem. Int. Ed.* **1980**, *19*, 520) which suggest a fluxional behavior of the ligands. A putative mechanism is depicted in Scheme S3.



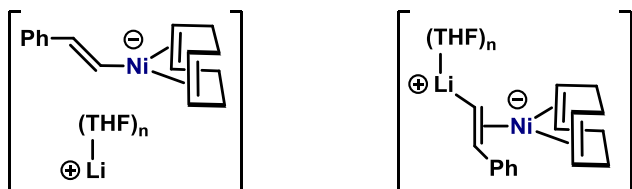
**Scheme S3**  
S6

*Oxidation state of the Nickel center:* The structure of complex **1** contains 3 largely elongated olefins bound to the Ni center with distances of 1.42, 1.46 and 1.47 Å. This experimental observation is in agreement to the Dewar-Chat-Duncanson model, in which the olefins can be described by the continuum from metallacyclopropane to olefin. Additionally, the Ni center is sharing electrons with the Li atom, thus making two metallic Ni–Li bonds, which indicates that electron density at the Ni is reserved to form two Li–Ni bonds. In the literature, these descriptions of Ni-olefin complexes usually refer to the dichotomy of Ni(0)-olefin/Ni(II) metallacyclopropane.<sup>2</sup> However, our case represents a two-fold down in oxidation state of this dichotomy and hence, a rare and unique form of a Ni(0) metallacyclopropane.

## 4 Stoichiometric Experiments



Other postulated structures for intermediate 20:



Scheme S4

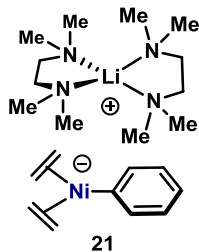
**Reaction A:** A Schlenk tube was charged with complex **1** (18.0 mg, 0.029 mmol) *via* argon trousers and dissolved in precooled THF (1 mL) at 0 °C. The solution was cooled to -78 °C and (*E*)-(2-bromovinyl)benzene (5.4 mg, 3.4 μL, 0.029 mmol, 1 eq.) was added *via* a Hamilton syringe. After stirring for 30 minutes, hexylMgBr (55 μL, 1.05 M, 0.058 mmol, 2 eq.) was added and the reaction was stirred overnight at -20 °C. The reaction was quenched with water and decane (10 μL, 7.3 mg, 0.051 mmol) was added as an internal standard. GC FID analysis showed 32 % product formation, along with styrene (15%) and substrate homocoupling (22%).

**Reaction B:** A Schlenk tube was charged with complex **1** (22.6 mg, 0.036 mmol) *via* argon trousers and dissolved in freshly dried (Na/K alloy) and precooled *d*<sub>8</sub>-THF (1 mL) at 0 °C. The solution was cooled to -78 °C and (*E*)-(2-bromovinyl)benzene (4.1 μL, 6.6 mg, 0.036 mmol, 1 eq.) was added *via* a Hamilton syringe. The reaction was stirred for 30 minutes, quenched by addition of water and rinsed with EtOAc. The qualitative amount of COD and styrene was determined by GC-FID to be 2:1.



## 5 Preparation of the Oxidative Addition Complex 21

In a Schlenk tube Ni(*trans,trans,trans*-cyclododecatriene) (150 mg, 0.68 mmol) was dissolved in freshly dried Et<sub>2</sub>O (5 mL). The Schlenk tube was cooled to -60 °C, and ethylene was bubbled through the solution for 5 minutes to ensure saturation. TMEDA (1.02 mL, 6.79 mmol, 10 eq.) and solid PhLi (63 mg, 0.75 mmol) were transferred to the reaction while maintaining 1 atm of ethylene bubbling through the solution. The reaction mixture was warmed to 0 °C and stirred for 15 minutes, after which ethylene bubbling was ceased. Precipitation formed during this period. The solution was separated from the formed solid *via* a glass cannula. The solid was dissolved in Et<sub>2</sub>O and cooled to -78 °C overnight, during which a powder precipitated. The solution was removed *via* a cannula and yielded the purified product (142 mg, 0.33 mmol, 48%) as a yellow solid.



<sup>1</sup>H NMR (-40 °C, 400 MHz, THF-*d*<sub>8</sub>) δ 7.53 (d, *J* = 7.0 Hz, 2H), 6.56 (t, *J* = 7.2 Hz, 2H), 6.35 (t, *J* = 7.0 Hz, 1H), 2.29 (s, 8H), 2.14 (s, 24H), 1.82 (s, 8H).

<sup>13</sup>C NMR (-40 °C, 101 MHz, THF-*d*<sub>8</sub>) δ 192.4, 141.8, 129.0, 123.8, 117.3, 58.7, 46.3.

<sup>7</sup>Li NMR (-40 °C, 156 MHz, THF-*d*<sub>8</sub>) δ -0.48 (s).

Attempts to crystallize compound **21** were unsuccessful. However, X-ray crystals of compound **22** could be obtained by dissolving the complex in Et<sub>2</sub>O at -20 °C and cooling to -50 °C over 3 days.

## 6 Procedure for Scheme 2

**Complex 1:** Reaction setup included a two-step process comprising stock solution preparation of complex **1** and its immediate use thereafter in the desired reaction. Accordingly, a small Schlenk tube was tared and an approximate amount of complex **1** (~0.01 mmol) was quickly transferred from the storage Schlenk tube *via* Ar trousers, while maintaining the storage Schlenk tube on dry ice (the exact weight of complex **1** was determined to calculate solvent dilution). The Schlenk was then placed in a precooled EtOH bath at  $-65\text{ }^{\circ}\text{C}$ . A second small Schlenk tube was charged with (*E*)-1-(2-bromovinyl)-4-methoxybenzene (~0.1 mmol). The substrate was dissolved in MTBE (0.2 M) at room temperature, and cooled to  $-65\text{ }^{\circ}\text{C}$ . HexylMgBr (0.15 mmol) was added as a solution in THF (1.05 M). Complex **1** in the first Schlenk tube was dissolved in precooled MTBE (0.2 M solution). After observing full solubility (taking the Schlenk out of the cooling bath and let it slightly warm up), complex **1** (5 mol%) was quickly transferred to the reaction. The vessel was sealed under a positive pressure of Ar and stirred at  $-65\text{ }^{\circ}\text{C}$  for 36 h. The reaction was quenched with  $\text{H}_2\text{O}$  and extracted ( $3\times$  EtOAc). The combined organic layers were dried with  $\text{MgSO}_4$  and evaporated under reduced pressure. Column chromatography (4:1 pentane: $\text{CH}_2\text{Cl}_2$ ), gave the pure product.

**Ni(0):** Reaction setup included a two-step process comprising stock solution preparation of the Ni(0) with Li-salt catalysts and its immediate use thereafter in the desired reaction. Accordingly, a small Schlenk tube was tared and an approximate amount of catalyst (~0.01 mmol) was quickly transferred from the storage Schlenk tube *via* Ar trousers (the exact weight of catalyst was determined to calculate solvent dilution). Based on the exact amount of  $\text{Ni}(\text{COD})_2$  weight in, the corresponding lithium salts (2 eq. in respect to the catalyst) were added as solids to the catalyst. A second small Schlenk tube was charged with (*E*)-1-(2-bromovinyl)-4-methoxybenzene (~0.1 mmol). The substrate was dissolved in MTBE (0.2 M), and cooled to  $-65\text{ }^{\circ}\text{C}$ . HexylMgBr (0.15 mmol) was added as a solution in THF (1.05 M). The catalyst with Li-salt in the first Schlenk tube was dissolved in MTBE (0.2 M catalyst solution) at room temperature. After observing full solubility, the catalyst mixture (5 mol%) was slowly added to the reaction. The vessel was sealed under a positive pressure of Ar and stirred at  $-65\text{ }^{\circ}\text{C}$  for 36 h. The reaction was quenched with  $\text{H}_2\text{O}$  and extracted ( $3\times$  EtOAc). The combined organic layers were dried with  $\text{MgSO}_4$  and evaporated under reduced pressure. GC-MS analysis of the residue showed no formation of product.

**$\text{NiCl}_2\text{dppe}$ :** A small Schlenk tube was charged with  $\text{NiCl}_2\text{dppe}$  (10.5 mg, 0.02 mmol, 10 mol%) and (*E*)-1-(2-bromovinyl)-4-methoxybenzene (42.6 mg, 0.2 mmol, 1 equiv.). The mixture was dissolved in MTBE

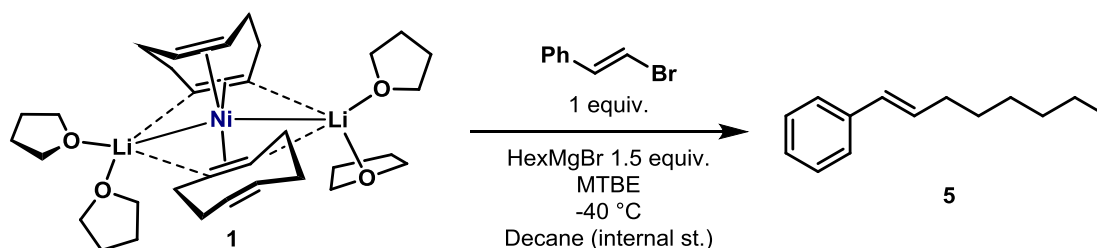
(0.2 M), and cooled to  $-65\text{ }^{\circ}\text{C}$ . HexylMgBr (285  $\mu\text{L}$ , 0.3 mmol, 1.5 equiv.) was added as a solution in THF (1.05 M). The vessel was sealed under a positive pressure of Ar and stirred at  $-65\text{ }^{\circ}\text{C}$  for 36 h. The reaction was quenched with  $\text{H}_2\text{O}$  and extracted ( $3\times$  EtOAc). The combined organic layers were dried with  $\text{MgSO}_4$  and evaporated under reduced pressure. Column chromatography (4:1 pentane: $\text{CH}_2\text{Cl}_2$ ), gave the pure product.

## 7 Kinetic Studies

Reaction setup included a two-step process comprising stock solution preparation of compound **1** and its immediate use thereafter in the desired reactions. Accordingly, a small Schlenk tube was tared and an approximate amount of complex **1** (~0.1 mmol) was quickly transferred from the storage Schlenk *via* Ar trousers, while maintaining the storage Schlenk on dry ice. The exact weight of complex **1** was determined to calculate solvent dilution and the Schlenk tube was placed in a precooled EtOH bath at  $-40\text{ }^{\circ}\text{C}$ .

A small Schlenk tube was charged with (*E*)-(2-bromovinyl)benzene (48.2 mg, 30  $\mu\text{L}$ , 0.263 mmol) and decane (18.3 mg, 25  $\mu\text{L}$ , 0.128 mmol) as internal standard. MTBE (0.2 M) was added and the reaction was cooled to  $-40\text{ }^{\circ}\text{C}$ . HexylMgBr (1.05 M; 370  $\mu\text{L}$ , 0.389 mmol, 1.5 eq.) was added as a solution in THF (1.05 M). Complex **1** in the first Schlenk tube was then dissolved in precooled MTBE (0.2 M solution). After observing full solubility, complex **1** (5 mol%) was quickly transferred to the reaction.

GC-FID samples were taken every minute and the reaction was afterwards stirred overnight (last data point).



Scheme S6

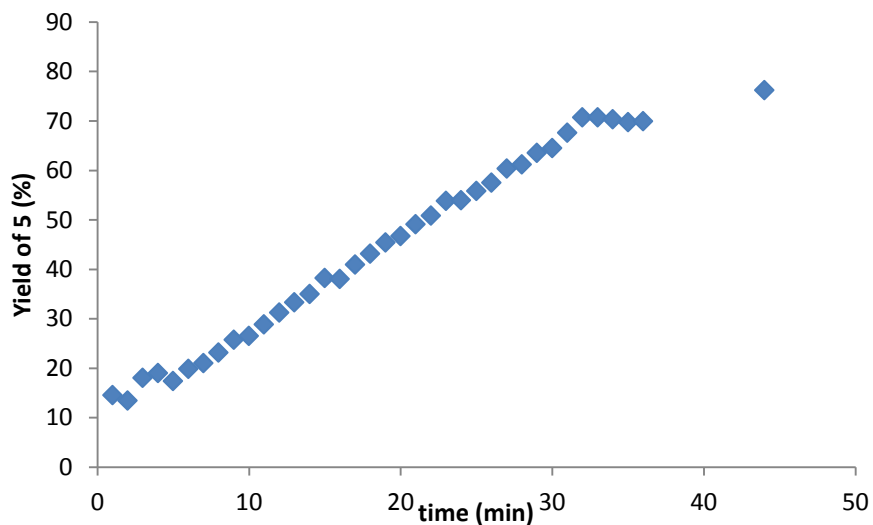


Figure S2

## 8 Procedures for Scheme 3

### *Catalytic Reaction:*

Reaction setup included a two-step process comprising stock solution preparation of compound **1** and its immediate use thereafter in the desired reaction. Accordingly, a small Schlenk tube was tared and an approximate amount of complex **1** (~0.01 mmol) was quickly transferred from the storage Schlenk tube *via* Ar trousers, while maintaining the storage Schlenk tube on dry ice (the exact weight of complex **1** was determined to calculate solvent dilution). The Schlenk was then placed in a precooled EtOH bath at 0 °C.

A second small Schlenk tube was charged with bromobenzene (~0.1 mmol), which was dissolved in THF (0.2 M), and cooled to 0 °C. HexylMgBr or MeLi (0.15 mmol) was added as a solution in THF (1.05 M – 2.0 M). Complex **1** in the first Schlenk tube was then dissolved in precooled THF (0.2 M solution). Complex **1** (5 mol%) was quickly transferred to the reaction Schlenk tube. This vessel was sealed under a positive pressure of Ar and stirred at 0 °C for 12 h.

The reaction was quenched with H<sub>2</sub>O and diluted with EtOAc. Dodecane was added as an internal standard and a GC-FID sample was prepared from the mixture to determine the yield. The coupling product was obtained in 18% when employing hexylMgBr (**3**) and 87% when employing MeLi (**24**) as a nucleophile.

### *Stoichiometric Reaction:*

Complex **21** was charged in a Schlenk tube, cooled to 0 °C and dissolved in precooled THF. The respective nucleophile (1 eq.) was added and the reaction was stirred at 0 °C overnight.

The reaction was quenched with H<sub>2</sub>O and diluted with EtOAc. Hexadecane was added as an internal standard and a GC-FID sample was prepared from the mixture to determine the yield. The coupling product was obtained in 10% when employing hexylMgBr (**3**) and 47% when employing MeLi (**24**) as a nucleophile.

## 9 Homogeneity Tests

### A) Hg drop test

Reaction setup included a two-step process comprising stock solution preparation of complex **1** and its immediate use thereafter in the desired reaction. Accordingly, a small Schlenk tube was tared and complex **1** (15.0 mg, 0.024 mmol) was quickly transferred from the storage Schlenk tube *via* Ar trousers, while maintaining the storage Schlenk tube on dry ice (the exact weight of complex **1** was determined to calculate solvent dilution). The Schlenk was then placed in a precooled EtOH bath at  $-20\text{ }^{\circ}\text{C}$ .

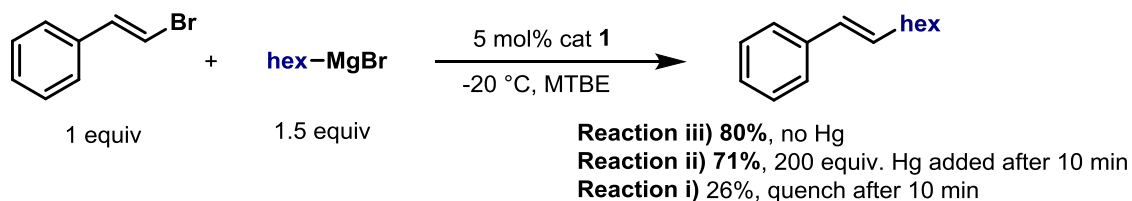
Three small Schlenk tubes were charged with (*E*)-(2-bromovinyl)benzene (29.4 mg, 0.161 mmol), which was dissolved in MTBE (1 mL), and cooled to  $-20\text{ }^{\circ}\text{C}$ . HexylMgBr (229  $\mu\text{L}$ , 0.241 mmol, 1.5 eq.) was added as a solution in THF (1.05 M). Complex **1** was then dissolved in precooled MTBE (1.8 mL for 3 reactions) and quickly distributed over the three reactions equally (5 mol% complex **1** loading for each reaction). The vessels were sealed under a positive pressure of Ar and stirred at  $-20\text{ }^{\circ}\text{C}$ .

**Reaction i):** The reaction was quenched with  $\text{H}_2\text{O}$  after 10 minutes, diluted with EtOAc and hexadecane (25  $\mu\text{L}$ , 19.3 mg, 0.085 mmol) was added as internal standard. The yield was determined by GC-FID to be 26%.

**Reaction ii)** Hg metal (28.8  $\mu\text{L}$ , 322 mg, 1.61 mmol, 200 eq. compared to complex **1**) was added to the reaction after 10 minutes *via* a Hamilton syringe. The stirring speed was increased to maximum speed of 1500 rpm. The reaction was quenched with  $\text{H}_2\text{O}$  after 12h, diluted with EtOAc and hexadecane (25  $\mu\text{L}$ , 19.3 mg, 0.085 mmol) was added as an internal standard. The yield was determined by GC-FID to be 71%.

**Reaction iii)** The reaction was quenched with  $\text{H}_2\text{O}$  after 12h, diluted with EtOAc and hexadecane (25  $\mu\text{L}$ , 19.3 mg, 0.085 mmol) was added as an internal standard. The yield was determined by GC-FID to be 80%.

Mercury drop-test in our system



Scheme S5

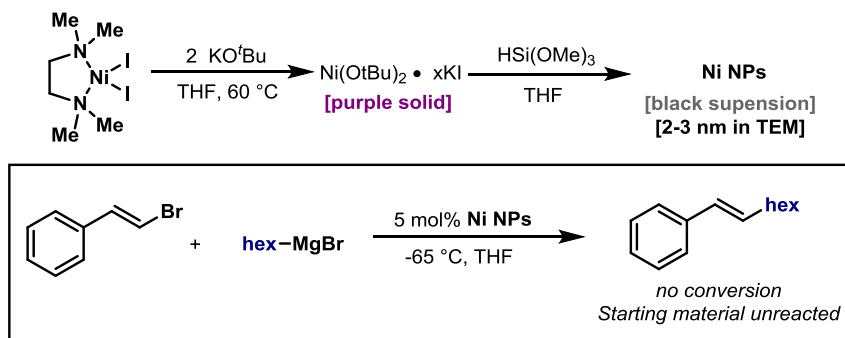
## B) Testing Ni-nanoparticles on catalytic activity under reaction conditions

Note: It is important to mention that Hu *et al.* have recently reported a Ni-catalyzed hydrosilylation of alkenes, which proceeds via the formation of active Ni nanoparticles (*Angew. Chem. Int. Ed.* **2016**, *55*, 12295). Interestingly, a Hg-drop test performed by the same group completely suppressed the reactivity of these nanoparticles, thus suggesting that amalgamation of Hg with Ni nanoparticles indeed occurred.

Ni-nanoparticles were prepared according to a described procedure by Hu *et al.*<sup>3</sup>

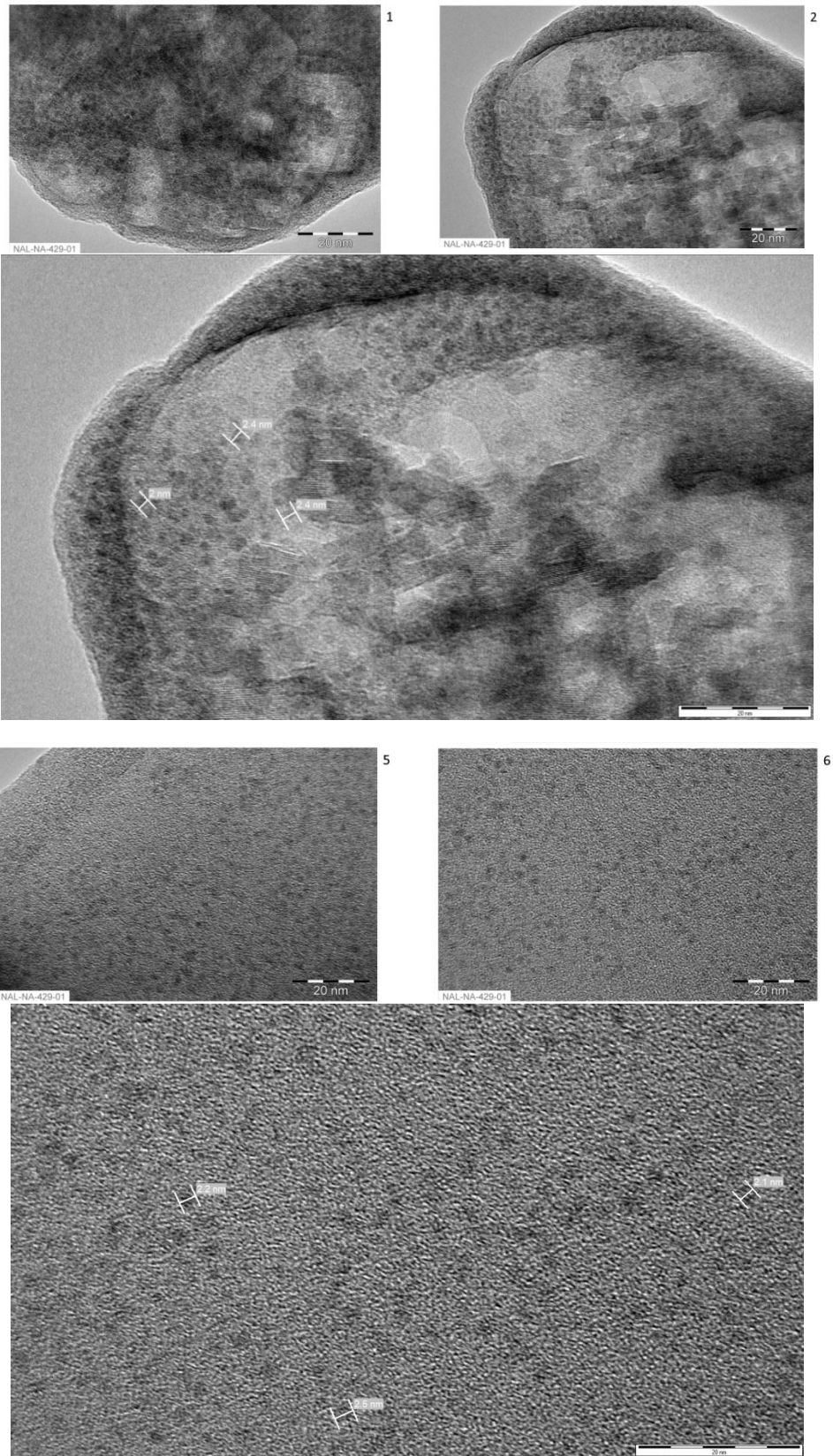
(E)-(2-bromovinyl)benzene (24.7 mg, 0.135 mmol) was dissolved in THF (350  $\mu$ L), cooled to  $-65$   $^{\circ}$ C and hexylMgBr (192  $\mu$ L, 0.202 mmol, 1.5 equiv., 1.05 M in THF) was added. The solution with Ni-nanoparticles (550 $\mu$ L in THF, accounting for 5% Ni-metal) was transferred to the reaction and the Schlenk was sealed under a positive pressure of argon. The reaction was quenched with water after 24h and analyzed by GC-MS. The coupling product could not be found.

Ni nanoparticles experiment following Hu's protocol



**Scheme S6**

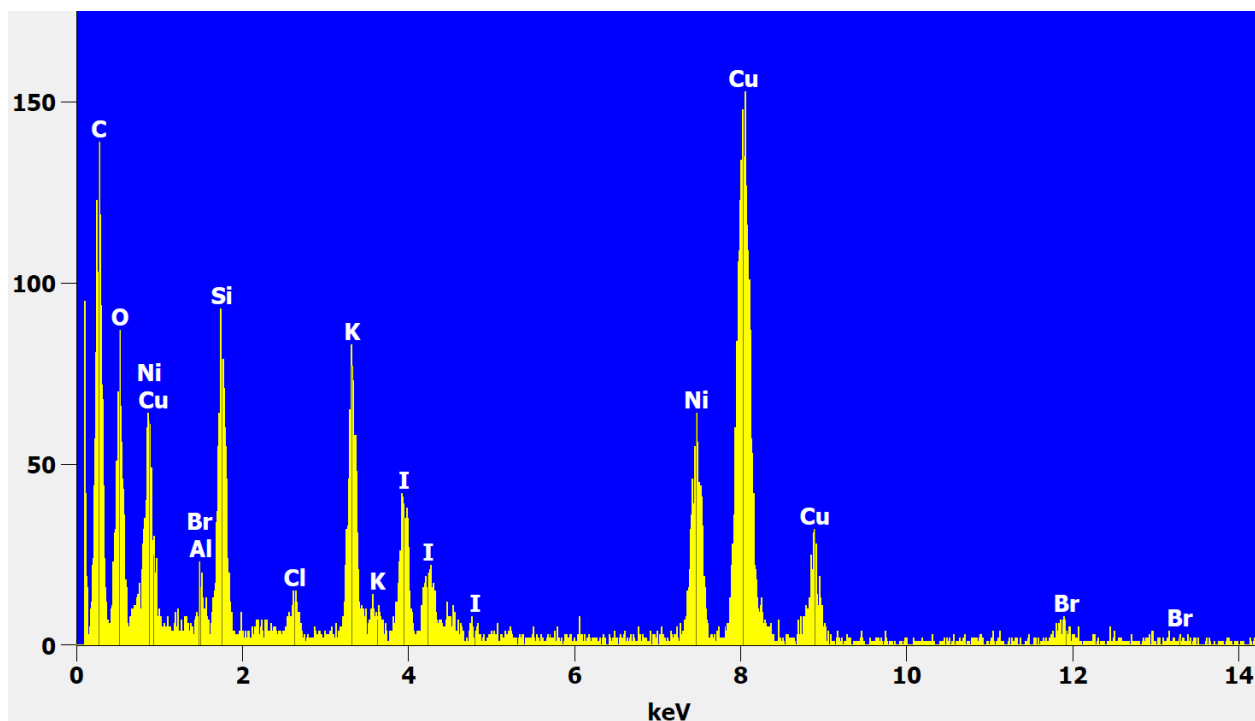
Taken together, these information points out at the lack of Ni-nanoparticles present in solution during our coupling reaction.



**Figure S3**

S16





Element Line	Weight %	Weight % Error	Atom %
O K	22.75	± 0.96	48.38
Al K	0.88	± 0.51	1.11
Si K	15.07	± 0.77	18.25
Cl K	2.82	± 0.45	2.70
K K	14.02	± 0.48	12.20
Ni K	16.21	± 1.15	9.39
Br K	2.52	± 0.73	1.07
I L	25.73	± 1.12	6.90
Total	100.00		100.00

**Figure S4**

The large amount of copper in the EDX refers to the Cu-grid on which the sample was prepared. The other identified atom species naturally represent the reagents used for the preparation of the Ni-nanoparticles and are indicative of the stoichiometry of the reaction.

Bromine, chlorine and aluminum can be considered impurities with 1.1%, 2.7% and 1.1% respectively over the overall atom percentage.

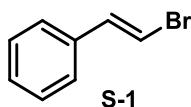
## 10 Starting Material Preparation

General Procedure A: adapted from Alexakis and coworkers.<sup>4</sup>

Step 1: The corresponding aldehyde (5 mmol) was charged in a Schlenk tube and dissolved in CH<sub>2</sub>Cl<sub>2</sub> (40 mL, 0.125 M). CBr<sub>4</sub> (2.48 g, 7.5 mmol, 1.5 eq.) was added and the mixture was cooled to 0 °C. PPh<sub>3</sub> (3.90 g, 15 mmol, 3 eq.) was added in portions over 30 minutes. After the last addition, the mixture was stirred for 1 h at 0 °C. The reaction was then evaporated under reduced pressure, dissolved in CHCl<sub>3</sub> and filtered over a glass-frit. The resulting solution was evaporated again under reduced pressure and subsequently purified by column chromatography to yield the dibromide, which was purified by flash column chromatography.

Step 2: Subsequently, the purified dibromide was charged in a round bottom flask and the atmosphere was replaced with argon by purging. Dimethylphosphite (1.64 g, 1.52 mL, 15 mmol, 3 eq.) was added and additionally a few drops of DMF if the dibromide was a solid. The reaction was cooled to 0 °C and triethylamine (1.517 g, 2.10 mL, 15 mmol, 3 eq.) was added dropwise. After addition, the reaction progress was monitored by TLC until completion (usually finished after 2h). The reaction was diluted with CH<sub>2</sub>Cl<sub>2</sub> and water was added. The aqueous layer was extracted (3 × CH<sub>2</sub>Cl<sub>2</sub>), the organic layers combined and dried with MgSO<sub>4</sub>. After purification by column chromatography the vinyl bromides were obtained in spectroscopic pure form.

### (*E*)-(2-Bromovinyl)benzene (S-1)



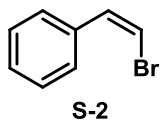
Prepared from β-bromostyrene, according to a literature procedure. Column chromatography (pentane) gave the product in analytically pure form. Spectroscopic data match those reported in the literature.<sup>4</sup>

$R_f$  (hexane) = 0.66

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.42 – 7.30 (m, 5H), 7.15 (d, *J* = 14.0 Hz, 1H), 6.81 (d, *J* = 14.0 Hz, 1H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 137.3, 136.0, 128.9, 128.4, 126.2, 106.7.

**(Z)-(2-Bromovinyl)benzene (S-2)**



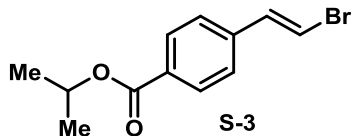
Prepared from cinnamic acid, according to a literature procedure. Column chromatography (pentane) gave the product in analytically pure form. Spectroscopic data match those reported in the literature.<sup>5</sup>

$R_f$  (hexane) = 0.66

$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.71 – 7.66 (m, 2H), 7.43 – 7.29 (m, 3H), 7.08 (d,  $J = 8.1$  Hz, 1H), 6.44 (d,  $J = 8.1$  Hz, 1H).

$^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  135.1, 132.5, 129.1, 128.5, 128.4, 106.5.

**(E)-Isopropyl 4-(2-bromovinyl)benzoate (S-3)**



Prepared from isopropyl 4-formylbenzoate (727 mg, 3.78 mmol), according to the General Procedure A. Column chromatography (hexane: $\text{CH}_2\text{Cl}_2$  5:1 to 1:1) gave the isolated product as colorless oil (499 mg, 49%). Spectroscopic data match those reported in the literature.<sup>6</sup>

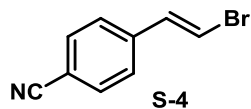
$R_f$  (hexane: $\text{CH}_2\text{Cl}_2$  1:1) = 0.50

*Major isomer (trans)*

$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.99 (d,  $J = 8.4$  Hz, 2H), 7.35 (d,  $J = 8.3$  Hz, 2H), 7.14 (d,  $J = 14.0$  Hz, 1H), 6.91 (d,  $J = 14.0$  Hz, 1H), 5.25 (p,  $J = 6.3$  Hz, 1H), 1.37 (d,  $J = 6.3$  Hz, 6H).

$^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  165.8, 140.0, 136.6, 130.6, 130.2, 126.0, 109.3, 68.7, 22.1.

**(E)-4-(2-Bromovinyl)benzonitrile (S-4)**



Prepared from 4-formylbenzonitrile (655 mg, 5 mmol), according to the General Procedure A. Column chromatography (hexane:CH<sub>2</sub>Cl<sub>2</sub> 5:1 to 1:1) gave the isolated product as colorless solid (390 mg, 37%). Spectroscopic data match those reported in the literature.<sup>7</sup>

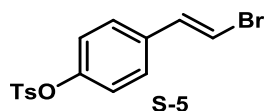
**R<sub>f</sub>** (hexane:CH<sub>2</sub>Cl<sub>2</sub> 1:1) = 0.50

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 7.63 (d, *J* = 8.3 Hz, 2H), 7.39 (d, *J* = 8.2 Hz, 2H), 7.13 (d, *J* = 14.1 Hz, 1H), 6.96 (d, *J* = 14.1 Hz, 1H).

**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 140.2, 135.8, 132.8, 126.7, 118.8, 111.8, 111.0.

**HRMS-EI:** calc'd for (C<sub>9</sub>H<sub>6</sub>N<sub>1</sub>Br<sub>1</sub>): 206.967824; found: 206.968150.

**4-(2-Bromovinyl)phenyl 4-methylbenzenesulfonate (S-5)**



Prepared from 4-formylphenyl 4-methylbenzenesulfonate (8.55 mmol, 2.4 g), according to the General Procedure A. Column chromatography (hexane:EtOAc 10:1 to 2:1) gave the isolated product as colorless solid (1.34 g, 44%, mixture of isomers).

**R<sub>f</sub>** (hexane:EtOAc 1:1) = 0.75

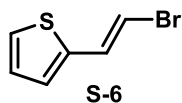
*Major isomer:*

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 7.73 – 7.68 (m, 2H), 7.34 – 7.29 (m, 2H), 7.23 – 7.18 (m, 2H), 7.04 (d, *J* = 14.1 Hz, 1H), 6.97 – 6.91 (m, 2H), 6.73 (d, *J* = 14.0 Hz, 1H), 2.45 (s, 3H).

**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 149.4, 145.6, 135.9, 135.0, 132.4, 129.9, 128.7, 127.4, 123.0, 107.7, 21.9.

**HRMS-ESI:** calc'd for (C<sub>15</sub>H<sub>13</sub>Br<sub>1</sub>O<sub>3</sub>S<sub>1</sub>Na<sub>1</sub>, M+Na<sup>+</sup>): 374.966112; found: 374.966250.

### 2-(2-Bromovinyl)thiophene (S-6)



Prepared from thiophene-2-carbaldehyde (560 mg, 5 mmol, 467  $\mu$ L), according to the General Procedure A. Column chromatography (hexane) gave the isolated product as a colorless oil (745 mg, 79%, mixture of isomers).

$R_f$  (hexane) = 0.62

*Major isomer:*

$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.31 – 7.24 (m, 2H), 7.08 – 7.03 (m, 2H), 6.71 (d,  $J$  = 14.1 Hz, 1H).

$^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  140.0, 130.4, 127.55, 126.2, 125.2, 105.3.

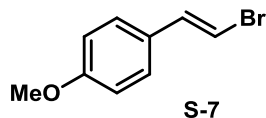
*Minor isomer:*

$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.47 (d,  $J$  = 5.1 Hz, 1H), 7.42 – 7.37 (m, 2H), 7.15 (m, 1H), 6.41 (d,  $J$  = 8.0 Hz, 1H).

$^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  138.3, 130.3, 127.0 (2C), 126.4, 104.3.

**HRMS-EI:** calc'd for ( $\text{C}_6\text{H}_5\text{Br}_1\text{S}_1$ ): 187.928998; found: 187.929230.

### (*E*)-1-(2-Bromovinyl)-4-methoxybenzene (S-7)



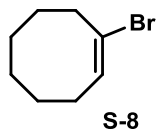
Prepared from 3-(4-methoxyphenyl)acrylic acid (1.950 g, 10.9 mmol), according to a literature procedure.<sup>8</sup> Column chromatography (pentane: $\text{CH}_2\text{Cl}_2$  4:1) gave the product as a colorless solid (1.84 g, 79%). Spectroscopic data match those reported in the literature.<sup>7</sup>

$R_f$  (pentane: $\text{CH}_2\text{Cl}_2$  4:1) = 0.28

$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.26 – 7.21 (m, 2H), 7.04 (d,  $J$  = 13.9 Hz, 1H), 6.88 – 6.83 (m, 2H), 6.61 (d,  $J$  = 13.9 Hz, 1H), 3.81 (s, 3H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  159.7, 136.6, 128.8, 127.4, 114.2, 104.0, 55.3.

**(E)-1-Bromocyclooct-1-ene (S-8)**



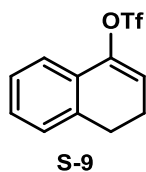
Cyclooctene (1.1 g, 10 mmol) was dissolved in  $\text{CH}_2\text{Cl}_2$  (4 mL) and cooled to 0 °C.  $\text{Br}_2$  (1.6 g, 512  $\mu\text{L}$ , 10 mmol, 1 eq.) was added dropwise and the reaction was stirred for 1 h at 0 °C. The reaction was quenched with sat. aq.  $\text{Na}_2\text{S}_2\text{O}_8$ , the aqueous layer was extracted ( $\text{CH}_2\text{Cl}_2 \times 3$ ) and the combined organic layers were dried with  $\text{MgSO}_4$ . After evaporation of the solvent under reduced pressure the crude dibromide was dissolved in THF (2 mL) and  $^t\text{BuOK}$  (1.7 g, 15 mmol, 1.5 eq.) was added slowly as a solution in THF (2 mL). The reaction was stirred overnight at room temperature and was then quenched with sat. aq.  $\text{NH}_4\text{Cl}$  solution. The aqueous layer was extracted ( $\text{CH}_2\text{Cl}_2 \times 3$ ) and the combined organic layers were dried with  $\text{MgSO}_4$ . The solvent was removed under reduced pressure and the crude product was purified by column chromatography (pentane) yielding the title compound (910 mg, 48 %) as colorless oil. Spectroscopic data match those reported in the literature.<sup>9</sup>

$R_f$  (pentane) = 0.75

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  6.03 (t,  $J = 8.5$  Hz, 1H), 2.64 – 2.58 (m, 2H), 2.13 – 2.06 (m, 2H), 1.67 – 1.59 (m, 2H), 1.58 – 1.47 (m, 6H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  131.8, 125.0, 35.3, 30.0, 28.8, 27.6, 26.6, 25.6.

**3,4-Dihydronaphthalen-1-yl trifluoromethanesulfonate (S-9)**



Prepared from 3,4-dihydronaphthalen-1(2H)-one, according to a literature procedure.<sup>10</sup> Column chromatography (pentane: $\text{CH}_2\text{Cl}_2$  20:1) gave the product as a colorless oil (208 mg, 20%). Spectroscopic data match those reported in the literature.<sup>10</sup>

$R_f$  (pentane:CH<sub>2</sub>Cl<sub>2</sub> 20:1) = 0.25

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.38 – 7.32 (m, 1H), 7.29 – 7.23 (m, 2H), 7.20 – 7.14 (m, 1H), 6.01 (t, *J* = 4.8 Hz, 1H), 2.87 (t, *J* = 8.2 Hz, 2H), 2.51 (td, *J* = 8.2, 4.8 Hz, 2H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 146.5, 136.6, 129.3, 128.8, 127.9, 127.1, 121.4, 118.8 (q, *J* = 320.0 Hz) 117.9, 27.0, 22.5.

## 11 Kumada Cross-Coupling catalyzed by Complex 1

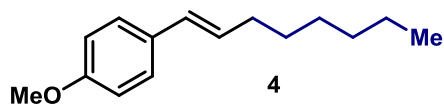
### General Procedure B:

Reaction setup included a two-step process comprising stock solution preparation of compound **1** and its immediate use thereafter in the desired reaction(s). Accordingly, a small Schlenk tube was tared and an approximate amount of complex **1** (~0.1 mmol) was quickly transferred from the storage Schlenk *via* Ar trousers, while maintaining the storage Schlenk on dry ice. The exact weight of complex **1** was determined to calculate solvent dilution and the Schlenk was placed in a precooled EtOH bath at the noted reaction temperature.

A second small Schlenk tube was charged with starting material (~0.3 mmol), which was dissolved in MTBE (0.2 M), and cooled to the noted temperature. The respective Grignard reagent (1.5 eq.) was added as a solution in THF or Et<sub>2</sub>O (1.05 M – 2.0 M). Complex **1** in the first Schlenk was then dissolved in precooled (–78 °C) MTBE (0.2 M solution) and the Schlenk was taken out of the cooling bath to accelerate the dissolving process (not exceeding a temperature elevation above –30 °C). After observing full solubility, the respective complex **1** (5-10 mol%) was quickly transferred to the reaction. This Schlenk was sealed under a positive pressure of Ar and stirred at the described temperature until conversion was observed by GCMS or TLC analysis.

The reaction was quenched with water and extracted with EtOAc for 3 times. The combined organic layers were dried with MgSO<sub>4</sub> and the solvent was evaporated under reduced pressure. Column chromatography or preparative TLC yielded the respective products.

### (*E*)-1-Methoxy-4-(oct-1-en-1-yl)benzene (**4**)



With Complex **1**: Following the General Procedure B at –65 °C with 5 mol% complex loading and hexylMgBr (1.05 M in THF), **4** was prepared from (*E*)-1-(2-bromovinyl)-4-methoxybenzene (31.5 mg, 0.148 mmol) in 36 h reaction time as a colorless oil (24.5 mg, 0.112 mmol, 76%). Spectroscopic data match those reported in the literature.<sup>11</sup>

With NiCl<sub>2</sub>(dppe): Following the Procedure for Scheme 2 (S11) at –65 °C with 5 mol% NiCl<sub>2</sub>(dppe) and hexylMgBr (1.05 M in THF), and (*E*)-1-(2-bromovinyl)-4-methoxybenzene (42.6 mg, 0.200 mmol). After



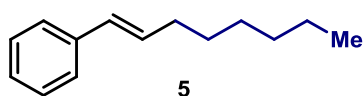
36 h, **4** was obtained as a colorless oil (13.0 mg, 0.059 mmol, 30%). Spectroscopic data match those reported in the literature.<sup>11</sup>

$R_f$  (pentane:CH<sub>2</sub>Cl<sub>2</sub> 4:1) = 0.45

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.32 – 7.24 (m, 2H), 6.89 – 6.80 (m, 2H), 6.33 (d, *J* = 15.8 Hz, 1H), 6.10 (dt, *J* = 15.8, 6.9 Hz, 1H), 3.82 (s, 3H), 2.20 (qd, *J* = 7.0, 1.5 Hz, 2H), 1.52 – 1.41 (m, 2H), 1.42 – 1.26 (m, 6H), 0.95 – 0.86 (m, 3H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 158.7, 131.0, 129.3, 129.1, 127.1, 114.0, 55.4, 33.2, 31.9, 29.7, 29.1, 22.8, 14.3.

#### (*E*)-Oct-1-en-1-ylbenzene (**5**)



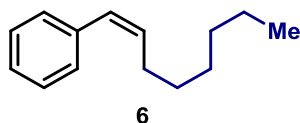
Following the General Procedure B at –65 °C with 5 mol% complex loading and hexylMgBr (1.05 M in THF), **5** was prepared from (*E*)-(2-bromovinyl)benzene (40.0 mg, 0.219 mmol) in 36 h reaction time as a colorless oil (27.4 mg, 0.146 mmol, 67%). Spectroscopic data match those reported in the literature.<sup>11</sup>

$R_f$  (pentane) = 0.60

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.36 – 7.32 (m, 2H), 7.31 – 7.27 (m, 2H), 7.19 (tt, *J* = 7.3, 1.3 Hz, 1H), 6.38 (d, *J* = 15.8 Hz, 1H), 6.23 (tt, *J* = 15.8, 6.8 Hz, 1H), 2.21 (qd, *J* = 7.0, 1.4 Hz, 2H), 1.52 – 1.42 (m, 2H), 1.39 – 1.24 (m, 6H), 0.92 – 0.87 (m, 3H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 138.1, 131.4, 129.8, 128.6, 126.9, 126.0, 33.2, 31.9, 29.5, 29.1, 22.8, 14.3.

#### (*Z*)-Oct-1-en-1-ylbenzene (**6**)



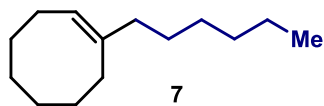
Following the General Procedure B at  $-20\text{ }^{\circ}\text{C}$  with 5 mol% complex loading and hexylMgBr (1.05 M in THF), **6** was prepared from (*Z*)-(2-bromovinyl)benzene (87.6 mg, 0.479 mmol) in 12 h reaction time as a colorless oil (60.7 mg, 0.322 mmol, 66%). Spectroscopic data match those reported in the literature.<sup>12</sup>

$R_f$  (pentane) = 0.60

$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.36 – 7.26 (m, 4H), 7.24 – 7.17 (m, 1H), 6.40 (dt,  $J = 11.7, 1.9$  Hz, 1H), 5.67 (dt,  $J = 11.7, 7.3$  Hz, 1H), 2.33 (qd,  $J = 7.3, 1.9$  Hz, 2H), 1.49 – 1.39 (m, 2H), 1.38 – 1.22 (m, 6H), 0.88 (t,  $J = 6.9$  Hz, 3H).

$^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  138.0, 133.4, 128.9, 128.8, 128.2, 126.5, 31.9, 30.1, 29.2, 28.8, 22.8, 14.2.

#### (*Z*)-1-Hexylcyclooct-1-ene (**7**)



Following the General Procedure B at  $-50\text{ }^{\circ}\text{C}$  with 10 mol% complex loading and hexylMgBr (1.05 M in THF), **7** was prepared from (*E*)-1-bromocyclooct-1-ene (37.1 mg, 0.196 mmol) in 24 h reaction time as a colorless oil (24 mg, 0.123 mmol, 63%). Purified by preparative TLC.

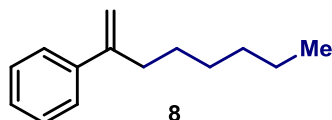
$R_f$  (hexane) = 0.95

$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  5.32 (tt,  $J = 8.1, 1.4$  Hz, 1H), 2.16 – 2.11 (m, 2H), 2.11 – 2.04 (m, 2H), 1.99 – 1.93 (m, 2H), 1.53 – 1.43 (m, 8H), 1.43 – 1.35 (m, 2H), 1.33 – 1.23 (m, 6H), 0.91 – 0.86 (m, 3H).

$^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  141.3, 123.5, 37.8, 32.0, 30.2, 29.5, 29.1, 29.1, 28.3, 26.7, 26.5, 26.4, 22.8, 14.3.

**HRMS-EI:** calc'd for  $\text{C}_{14}\text{H}_{26}$  [M]: 194.202900; found: 194.202820.

#### Oct-1-en-2-ylbenzene (**8**)



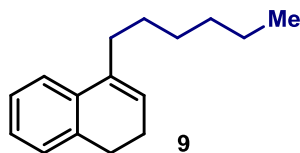
Following the General Procedure B at  $-20\text{ }^{\circ}\text{C}$  with 5 mol% complex loading and hexylMgBr (1.05 M in THF), **8** was prepared from (1-bromovinyl)benzene (54.1 mg, 0.296 mmol) in 12 h reaction time as a colorless oil (28.9 mg, 0.153 mmol, 52%). Spectroscopic data match those reported in the literature.<sup>13</sup>

$R_f$  (pentane) = 0.70

$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.43 – 7.39 (m, 2H), 7.35 – 7.29 (m, 2H), 7.28 – 7.23 (m, 1H), 5.26 (d,  $J$  = 1.6 Hz, 1H), 5.05 (q,  $J$  = 1.4 Hz, 1H), 2.50 (td,  $J$  = 7.7, 1.0 Hz, 2H), 1.50 – 1.39 (m, 2H), 1.37 – 1.22 (m, 6H), 0.91 – 0.83 (m, 3H).

$^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  149.0, 141.7, 128.4, 127.4, 126.3, 112.1, 35.5, 31.8, 29.2, 28.4, 22.8, 14.2.

#### 4-Hexyl-1,2-dihydronaphthalene (**9**)



Following the General Procedure B at  $-50\text{ }^{\circ}\text{C}$  with 10 mol% complex loading and hexylMgBr (1.05 M in THF), **9** was prepared from 3,4-dihydronaphthalen-1-yl trifluoromethanesulfonate (53.5 mg, 0.192 mmol) in 24 h reaction time as a colorless oil (20.7 mg, 0.097 mmol, 50%).

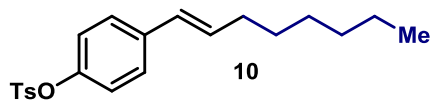
$R_f$  (pentane) = 0.55

$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.27 – 7.23 (m, 1H), 7.22 – 7.17 (m, 1H), 7.15 – 7.11 (m, 2H), 5.85 (t,  $J$  = 4.4 Hz, 1H), 2.74 (t,  $J$  = 8.0 Hz, 2H), 2.46 – 2.39 (m, 2H), 2.28 – 2.22 (m, 2H), 1.57 – 1.48 (m, 2H), 1.41 – 1.25 (m, 6H), 0.92 – 0.87 (m, 3H).

$^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  137.0, 136.8, 135.2, 127.7, 126.6, 126.4, 124.7, 122.8, 32.9, 31.9, 29.5, 28.7, 28.6, 23.3, 22.8, 14.3.

**HRMS-EI:** calc'd for  $\text{C}_{16}\text{H}_{22}$  [M]: 214.171600; found: 214.171490.

**(E)-4-(Oct-1-en-1-yl)phenyl 4-methylbenzenesulfonate (10)**



With complex **1**: Following the General Procedure B at  $-65\text{ }^{\circ}\text{C}$  with 10 mol% complex loading and hexylMgBr (1.05 M in THF), **10** was prepared from (E)-4-(2-bromovinyl)phenyl 4-methylbenzenesulfonate (70.9 mg, 0.200 mmol) in 36 h reaction time as a colorless oil (43.7 mg, 0.122 mmol, 61%).

With  $\text{NiCl}_2(\text{dppe})$ : Following the Procedure for Scheme 2 (S11) at  $-65\text{ }^{\circ}\text{C}$  with 10 mol%  $\text{NiCl}_2(\text{dppe})$ , hexylMgBr (1.05 M in THF) and (E)-4-(2-bromovinyl)phenyl 4-methylbenzenesulfonate. No product formation was observed after 36 h.

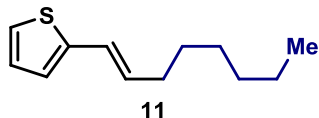
$R_f$  (hexane:EtOAc 19:1) = 0.30

$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.72 – 7.68 (m, 2H), 7.32 – 7.28 (m, 2H), 7.24 – 7.20 (m, 2H), 6.91 – 6.86 (m, 2H), 6.33 – 6.27 (m, 1H), 6.17 (dt,  $J = 15.8, 6.8$  Hz, 1H), 2.44 (s, 3H), 2.23 – 2.12 (m, 2H), 1.43 (m, 2H), 1.37 – 1.22 (m, 6H), 0.92 – 0.83 (m, 3H).

$^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  148.4, 145.4, 137.1, 134.3, 132.6, 129.9, 128.7, 128.5, 127.0, 122.5, 33.2, 31.9, 29.4, 29.0, 22.8, 21.9, 14.3.

**HRMS-EI**: calc'd for  $\text{C}_{21}\text{H}_{26}\text{O}_3\text{SNa}$  [ $\text{M}+\text{Na}^+$ ]: 381.149487; found: 381.149570.

**2-(Oct-1-en-1-yl)thiophene (11)**



Following the General Procedure B at  $-65\text{ }^{\circ}\text{C}$  with 10 mol% complex loading and hexylMgBr (1.05 M in THF), **11** was prepared from 2-(2-bromovinyl)thiophene (35.8 mg, 0.190 mmol) in 36 h reaction time as a colorless oil (18.0 mg, 0.093 mmol, 49%). Spectroscopic data match those reported in the literature.<sup>14</sup>

$R_f$  (pentane) = 0.61

Major isomer (*trans*)

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 7.08 (d, *J* = 5.1 Hz, 1H), 6.93 (dd, *J* = 5.1, 3.5 Hz, 1H), 6.86 (dd, *J* = 3.6, 1.0 Hz, 1H), 6.50 (d, *J* = 15.6 Hz, 1H), 6.07 (dt, *J* = 15.6, 7.0 Hz, 1H), 2.17 (qd, *J* = 7.1, 1.5 Hz, 2H), 1.49 – 1.41 (m, 2H), 1.39 – 1.24 (m, 6H), 0.93 – 0.86 (m, 3H).

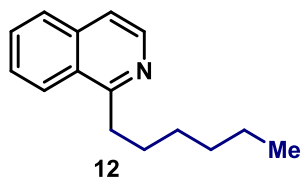
**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 143.2, 131.3, 127.2, 124.1, 123.0, 122.9, 32.9, 31.7, 29.2, 28.9, 22.6, 14.1.

*Minor isomer (cis)*

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 7.25 – 7.23 (m, 1H), 7.00 (dd, *J* = 5.1, 3.6 Hz, 1H), 6.97 (dd, *J* = 3.7, 1.1 Hz, 1H), 6.56 – 6.53 (m, 1H), 5.59 (dt, *J* = 11.5, 7.2 Hz, 1H), 2.41 (qd, *J* = 7.3, 1.9 Hz, 2H), 1.50 – 1.41 (m, 2H), 1.37 – 1.23 (m, 6H), 0.93 – 0.84 (m, 3H).

The carbon signals for the cis product could not be accurately assigned from the mixture.

### 1-Hexylisoquinoline (**12**)



Following the General Procedure B at –50 °C with 5 mol% complex loading and hexylMgBr (1.05 M in THF), **12** was prepared from 1-chloroisoquinoline (47.3 mg, 0.289 mmol) in 72 h reaction time as a yellow oil (37.2 mg, 0.174 mmol, 60%).

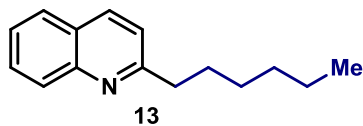
**R<sub>f</sub>** (hexane:EtOAc 5:1) = 0.55

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 8.43 (d, *J* = 5.7 Hz, 1H), 8.16 (dq, *J* = 8.4, 1.0 Hz, 1H), 7.81 (dt, *J* = 8.2, 0.9 Hz, 1H), 7.66 (ddd, *J* = 8.1, 6.8, 1.3 Hz, 1H), 7.58 (ddd, *J* = 8.3, 6.9, 1.4 Hz, 1H), 7.49 (dd, *J* = 5.7, 0.9 Hz, 1H), 3.35 – 3.24 (m, 2H), 1.91 – 1.80 (m, 2H), 1.53 – 1.43 (m, 2H), 1.41 – 1.27 (m, 4H), 0.93 – 0.83 (m, 3H).

**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 162.6, 142.0, 136.4, 129.9, 127.5, 127.0 (2), 125.5, 119.2, 35.8, 31.9, 30.0, 29.8, 22.8, 14.2.

**HRMS-ESI:** calc'd for C<sub>15</sub>H<sub>20</sub>N [M+H<sup>+</sup>]: 214.159024; found: 214.159020.

### 2-Hexylquinoline (**13**)



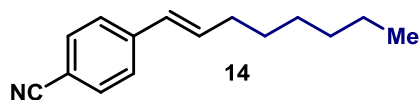
Following the General Procedure B at  $-20\text{ }^{\circ}\text{C}$  with 5 mol% complex loading and hexylMgBr (1.05 M in THF), **13** was prepared from 2-chloroquinoline (31.8 mg, 0.192 mmol) or 2-fluoroquinoline (49.6 mg, 0.337 mmol) in 12 h reaction time as a yellow oil (from chloro: 28.9 mg, 0.135 mmol, 70%), (from fluoro: 29.3 mg, 0.137 mmol, 41%). Spectroscopic data match those reported in the literature.<sup>15</sup>

$R_f$  (hexane:EtOAc 5:1) = 0.61

$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.05 (dd,  $J = 8.4, 1.7$  Hz, 2H), 7.76 (dd,  $J = 8.0, 1.4$  Hz, 1H), 7.67 (ddd,  $J = 8.5, 6.9, 1.5$  Hz, 1H), 7.47 (ddd,  $J = 8.1, 6.9, 1.2$  Hz, 1H), 7.29 (d,  $J = 8.5$  Hz, 1H), 3.01 – 2.92 (m, 2H), 1.86 – 1.75 (m, 2H), 1.48 – 1.38 (m, 2H), 1.37 – 1.27 (m, 4H), 0.92 – 0.85 (m, 3H).

$^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  163.1, 148.0, 136.1, 129.3, 128.8, 127.5, 126.7, 125.6, 121.4, 39.4, 31.8, 30.1, 29.3, 22.6, 14.1.

### (*E*)-4-(Oct-1-en-1-yl)benzonitrile (**14**)



With complex **1**: Following the General Procedure B at  $-50\text{ }^{\circ}\text{C}$  with 10 mol% complex loading and hexylMgBr (1.05 M in THF), **14** was prepared from (*E*)-4-(2-bromovinyl)benzonitrile (43.8 mg, 0.211 mmol) in 24 h reaction time as a colorless oil (23.0 mg, 0.108 mmol, 51%).

With  $\text{NiCl}_2(\text{dppe})$ : Following the Procedure for Scheme 2 (S11) at  $-50\text{ }^{\circ}\text{C}$  with 10 mol%  $\text{NiCl}_2(\text{dppe})$  and hexylMgBr (1.05 M in THF) and (*E*)-4-(2-bromovinyl)benzonitrile (41.6 mg, 0.200 mmol). After 24 h, **14** was obtained as a colorless oil (21.5 mg, 0.101 mmol, 50%).

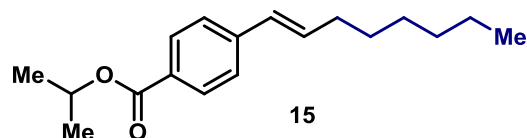
$R_f$  (hexane:EtOAc 19:1) = 0.45

$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.58 – 7.54 (m, 2H), 7.43 – 7.37 (m, 2H), 6.40 – 6.36 (m, 2H), 2.24 (m, 2H), 1.52 – 1.41 (m, 2H), 1.39 – 1.23 (m, 6H), 0.89 (td,  $J = 6.0, 5.2, 2.3$  Hz, 3H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  142.6, 135.8, 132.5, 128.5, 126.5, 119.3, 110.1, 33.3, 31.8, 29.2, 29.1, 22.8, 14.2.

**HRMS-EI:** calc'd for  $\text{C}_{15}\text{H}_{19}\text{N}$  [M]: 213.151199; found: 213.151280.

### Isopropyl (*E*)-4-(oct-1-en-1-yl)benzoate (**15**)



With complex **1**: Following the General Procedure B at  $-50\text{ }^\circ\text{C}$  with 10 mol% complex loading and hexylMgBr (1.05 M in THF), **15** was prepared from isopropyl (*E*)-4-(2-bromovinyl)benzoate (56.6 mg, 0.211 mmol) in 24 h reaction time as a colorless oil (38.0 mg, 0.138 mmol, 66%).

With  $\text{NiCl}_2(\text{dppe})$ : Following the Procedure for Scheme 2 (S11) at  $-50\text{ }^\circ\text{C}$  with 10 mol%  $\text{NiCl}_2(\text{dppe})$ , hexylMgBr (1.05 M in THF) and (*E*)-4-(2-bromovinyl)benzoate (56.6 mg, 0.211 mmol). No product formation was observed after 24h.

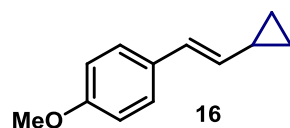
$R_f$  (hexane:EtOAc 19:1) = 0.28

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.95 (d,  $J = 8.4$  Hz, 2H), 7.38 (d,  $J = 8.4$  Hz, 2H), 6.46 – 6.30 (m, 2H), 5.24 (hept,  $J = 6.2$  Hz, 1H), 2.28 – 2.19 (m, 2H), 1.53 – 1.42 (m, 2H), 1.36 (d,  $J = 6.2$  Hz, 6H), 1.34 – 1.26 (m, 6H), 0.93 – 0.87 (m, 3H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  166.2, 142.4, 134.2, 129.9, 129.5, 129.2, 125.8, 68.3, 33.3, 31.9, 29.3, 29.1, 22.8, 22.1, 14.3.

**HRMS-ESI:** calc'd for  $\text{C}_{18}\text{H}_{26}\text{O}_2\text{Na}$  [ $\text{M}+\text{Na}^+$ ]: 297.182499; found: 297.182410.

### (*E*)-1-(2-Cyclopropylvinyl)-4-methoxybenzene (**16**)



Following the General Procedure B at  $-50\text{ }^{\circ}\text{C}$  with 5 mol% complex loading, **16** was prepared from (*E*)-1-(2-bromovinyl)-4-methoxybenzene (61.6 mg, 0.289 mmol) and cyclopropylMgBr (1 M in Et<sub>2</sub>O), in 24 h reaction time as a colorless solid (30.7 mg, 0.176 mmol, 61%).

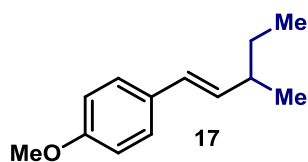
$R_f$  (hexane:CH<sub>2</sub>Cl<sub>2</sub> 4:1) = 0.25

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.27 – 7.22 (m, 2H), 6.87 – 6.80 (m, 2H), 6.43 (d,  $J$  = 15.7 Hz, 1H), 5.62 (dd,  $J$  = 15.7, 8.8 Hz, 1H), 3.80 (s, 3H), 1.60 – 1.49 (m, 1H), 0.86 – 0.76 (m, 1H), 0.50 (dt,  $J$  = 6.5, 4.5 Hz, 3H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  158.6, 132.7, 130.8, 126.9, 126.8, 114.0, 55.4, 14.6, 7.2.

HRMS-EI: calc'd for C<sub>12</sub>H<sub>14</sub>O [M]: 174.103915; found: 174.104070.

#### (*E*)-1-Methoxy-4-(3-methylpent-1-en-1-yl)benzene (**17**)



Following the General Procedure B at  $-50\text{ }^{\circ}\text{C}$  with 5 mol% complex loading and <sup>s</sup>BuMgCl (2 M in Et<sub>2</sub>O), **17** was prepared from (*E*)-1-(2-bromovinyl)-4-methoxybenzene (52.0 mg, 0.244 mmol) in 24 h reaction time as a colorless oil (24.1 mg, 0.127 mmol, 52%).

$R_f$  (hexane:CH<sub>2</sub>Cl<sub>2</sub> 4:1) = 0.29

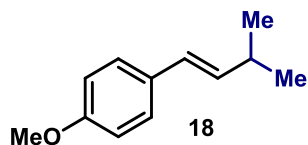
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.32 – 7.27 (m, 2H), 6.88 – 6.80 (m, 2H), 6.29 (d,  $J$  = 15.9, 1H), 5.96 (dd,  $J$  = 15.8, 7.9 Hz, 1H), 3.80 (s, 3H), 2.24 – 2.12 (m, 1H), 1.45 – 1.36 (m, 2H), 1.07 (d,  $J$  = 6.7 Hz, 3H), 0.91 (t,  $J$  = 7.4 Hz, 3H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  158.7, 134.8, 131.0, 127.6, 127.1, 114.0, 55.4, 39.0, 30.1, 20.5, 12.0.

HRMS-EI: calc'd for C<sub>13</sub>H<sub>18</sub>O [M]: 190.135215; found: 190.135410.



**(E)-1-Methoxy-4-(3-methylbut-1-en-1-yl)benzene (18)**



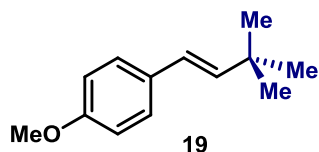
Following the General Procedure B at  $-50\text{ }^{\circ}\text{C}$  with 5 mol% complex loading and  ${}^t\text{PrMgCl}$  (2 M in  $\text{Et}_2\text{O}$ ), **18** was prepared from (E)-1-(2-bromovinyl)-4-methoxybenzene (52.0 mg, 0.244 mmol) in 24 h as a colorless oil (36.4 mg, 0.207 mmol, 85%). Spectroscopic data matched those reported in the literature.<sup>16</sup>

$R_f$ (hexane: $\text{CH}_2\text{Cl}_2$  4:1) = 0.28

${}^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.28 (m, 2H), 6.86 – 6.81 (m, 2H), 6.29 (dd,  $J = 15.8, 1.2$  Hz, 1H), 6.06 (dd,  $J = 15.9, 6.8$  Hz, 1H), 3.80 (s, 3H), 2.44 (dhep,  $J = 6.7, 1.3$  Hz, 1H), 1.09 (d,  $J = 6.7$  Hz, 6H).

${}^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  158.8, 136.1, 130.9, 127.2, 126.3, 114.0, 55.4, 31.6, 22.7.

**(E)-1-(3,3-Dimethylbut-1-en-1-yl)-4-methoxybenzene (19)**



Following the General Procedure B at  $-50\text{ }^{\circ}\text{C}$  with 10 mol% complex loading and  ${}^t\text{BuMgCl}$  (2 M in  $\text{Et}_2\text{O}$ ), **19** was prepared from (E)-1-(2-bromovinyl)-4-methoxybenzene (41.7 mg, 0.196 mmol) in 24 h reaction time as a colorless oil (13.9 mg, 0.073 mmol, 37%). Spectroscopic data matched those reported in the literature.<sup>16</sup>

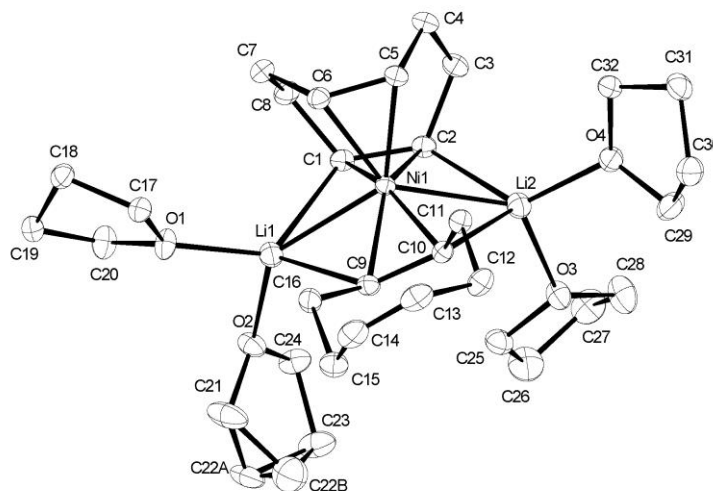
$R_f$ (hexane: $\text{CH}_2\text{Cl}_2$  4:1) = 0.28

${}^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.32 – 7.27 (m, 2H), 6.86 – 6.82 (m, 2H), 6.25 (d,  $J = 16.2$  Hz, 1H), 6.12 (d,  $J = 16.2$  Hz, 1H), 3.80 (s, 3H), 1.11 (s, 9H).

${}^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  158.7, 140.0, 131.0, 127.2, 124.0, 114.1, 55.4, 33.4, 29.9.

## 12 X-Ray characterization

### Complex 1:



**Table 1. Crystal data and structure refinement.**

Identification code	10882
Empirical formula	$C_{32}H_{56}Li_2NiO_4$
Color	orange
Formula weight	$577.35 \text{ g} \cdot \text{mol}^{-1}$
Temperature	100(2) K
Wavelength	$0.71073 \text{ \AA}$
Crystal system	MONOCLINIC
Space group	<b><math>P2_1/c</math>, (no. 14)</b>
Unit cell dimensions	$a = 10.5241(13) \text{ \AA}$ $\alpha = 90^\circ$ . $b = 18.135(2) \text{ \AA}$ $\beta = 107.478(2)^\circ$ . $c = 17.197(2) \text{ \AA}$ $\gamma = 90^\circ$ .

Volume	3130.6(7) Å <sup>3</sup>	
Z	4	
Density (calculated)	1.225 Mg · m <sup>-3</sup>	
Absorption coefficient	0.653 mm <sup>-1</sup>	
F(000)	1256 e	
Crystal size	0.382 x 0.262 x 0.222 mm <sup>3</sup>	
θ range for data collection	2.483 to 33.204°.	
Index ranges	-16 ≤ h ≤ 16, -27 ≤ k ≤ 27, -26 ≤ l ≤ 26	
Reflections collected	103179	
Independent reflections	11960 [R <sub>int</sub> = 0.0231]	
Reflections with I > 2σ(I)	10590	
Completeness to θ = 25.242°	99.9 %	
Absorption correction	Gaussian	
Max. and min. transmission	0.90 and 0.85	
Refinement method	Full-matrix least-squares on F <sup>2</sup>	
Data / restraints / parameters	11960 / 0 / 364	
Goodness-of-fit on F <sup>2</sup>	1.047	
Final R indices [I > 2σ(I)]	R <sub>1</sub> = 0.0290	wR <sup>2</sup> = 0.0764
R indices (all data)	R <sub>1</sub> = 0.0350	wR <sup>2</sup> = 0.0807
Largest diff. peak and hole	1.2 and -0.4 e · Å <sup>-3</sup>	

**Table 2. Bond lengths [ $\text{\AA}$ ] and angles [ $^\circ$ ].**

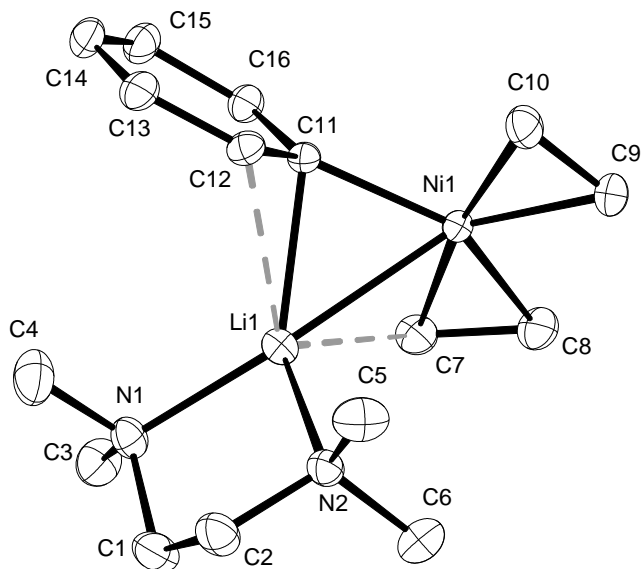
---

Ni(1)-C(1)	1.9865(9)	Ni(1)-C(2)	1.9997(8)
Ni(1)-C(5)	2.0449(8)	Ni(1)-C(6)	2.0596(9)
Ni(1)-C(9)	2.0007(8)	Ni(1)-C(10)	1.9754(9)
Ni(1)-Li(1)	2.4171(17)	Ni(1)-Li(2)	2.4184(17)
O(1)-C(17)	1.4473(10)	O(1)-C(20)	1.4484(11)
O(1)-Li(1)	1.9628(18)	O(2)-C(21)	1.4381(13)
O(2)-C(24)	1.4410(11)	O(2)-Li(1)	1.9829(18)
O(3)-C(25)	1.4439(12)	O(3)-C(28)	1.4419(12)
O(3)-Li(2)	1.9795(18)	O(4)-C(29)	1.4433(13)
O(4)-C(32)	1.4461(11)	O(4)-Li(2)	1.9324(18)
C(1)-C(2)	1.4635(12)	C(1)-C(8)	1.5369(13)
C(2)-C(3)	1.5277(12)	C(3)-C(4)	1.5470(13)
C(4)-C(5)	1.5275(12)	C(5)-C(6)	1.4198(12)
C(6)-C(7)	1.5232(13)	C(7)-C(8)	1.5458(13)
C(9)-C(10)	1.4735(12)	C(9)-C(16)	1.5248(12)
C(10)-C(11)	1.5196(12)	C(10)-Li(2)	2.2978(19)
C(11)-C(12)	1.5645(13)	C(12)-C(13)	1.5050(14)
C(13)-C(14)	1.3311(17)	C(14)-C(15)	1.4989(16)
C(15)-C(16)	1.5677(13)	C(16)-Li(1)	2.766(2)
C(17)-C(18)	1.5164(13)	C(18)-C(19)	1.5278(13)
C(19)-C(20)	1.5075(13)	C(21)-C(22A)	1.5209(18)
C(21)-C(22B)	1.562(6)	C(22A)-C(23)	1.4946(19)
C(22B)-C(23)	1.435(6)	C(23)-C(24)	1.5125(15)
C(25)-C(26)	1.5186(15)	C(26)-C(27)	1.5273(19)
C(27)-C(28)	1.5014(17)	C(29)-C(30)	1.5128(16)
C(30)-C(31)	1.5237(15)	C(31)-C(32)	1.5205(14)
C(1)-Ni(1)-C(2)	43.08(4)	C(1)-Ni(1)-C(5)	96.69(3)
C(1)-Ni(1)-C(6)	85.99(4)	C(1)-Ni(1)-C(9)	122.99(4)
C(1)-Ni(1)-Li(1)	65.79(5)	C(1)-Ni(1)-Li(2)	103.57(5)
C(2)-Ni(1)-C(5)	85.97(3)	C(2)-Ni(1)-C(6)	104.25(4)
C(2)-Ni(1)-C(9)	138.30(4)	C(2)-Ni(1)-Li(1)	104.92(5)

C(2)-Ni(1)-Li(2)	63.42(5)	C(5)-Ni(1)-C(6)	40.47(3)
C(5)-Ni(1)-Li(1)	128.92(5)	C(5)-Ni(1)-Li(2)	96.12(5)
C(6)-Ni(1)-Li(1)	89.04(5)	C(6)-Ni(1)-Li(2)	136.59(5)
C(9)-Ni(1)-C(5)	134.10(4)	C(9)-Ni(1)-C(6)	114.39(4)
C(9)-Ni(1)-Li(1)	62.29(5)	C(9)-Ni(1)-Li(2)	95.80(5)
C(10)-Ni(1)-C(1)	152.26(4)	C(10)-Ni(1)-C(2)	124.76(4)
C(10)-Ni(1)-C(5)	107.96(4)	C(10)-Ni(1)-C(6)	121.07(3)
C(10)-Ni(1)-C(9)	43.50(3)	C(10)-Ni(1)-Li(1)	105.63(5)
C(10)-Ni(1)-Li(2)	62.10(5)	Li(1)-Ni(1)-Li(2)	133.75(6)
C(17)-O(1)-C(20)	109.12(7)	C(17)-O(1)-Li(1)	126.75(7)
C(20)-O(1)-Li(1)	119.98(7)	C(21)-O(2)-C(24)	108.54(7)
C(21)-O(2)-Li(1)	120.50(8)	C(24)-O(2)-Li(1)	123.37(8)
C(25)-O(3)-Li(2)	112.76(8)	C(28)-O(3)-C(25)	108.75(8)
C(28)-O(3)-Li(2)	125.07(9)	C(29)-O(4)-C(32)	109.35(7)
C(29)-O(4)-Li(2)	119.96(8)	C(32)-O(4)-Li(2)	121.51(8)
C(2)-C(1)-Ni(1)	68.94(5)	C(2)-C(1)-C(8)	120.25(7)
C(8)-C(1)-Ni(1)	114.00(6)	C(1)-C(2)-Ni(1)	67.98(5)
C(1)-C(2)-C(3)	120.56(8)	C(3)-C(2)-Ni(1)	113.22(6)
C(2)-C(3)-C(4)	112.16(7)	C(5)-C(4)-C(3)	112.67(7)
C(4)-C(5)-Ni(1)	112.31(6)	C(6)-C(5)-Ni(1)	70.32(5)
C(6)-C(5)-C(4)	121.45(8)	C(5)-C(6)-Ni(1)	69.21(5)
C(5)-C(6)-C(7)	120.91(8)	C(7)-C(6)-Ni(1)	111.28(6)
C(6)-C(7)-C(8)	112.53(7)	C(1)-C(8)-C(7)	112.09(7)
C(10)-C(9)-Ni(1)	67.34(5)	C(10)-C(9)-C(16)	120.59(7)
C(16)-C(9)-Ni(1)	125.39(6)	Ni(1)-C(10)-Li(2)	68.46(5)
C(9)-C(10)-Ni(1)	69.17(5)	C(9)-C(10)-C(11)	121.60(7)
C(9)-C(10)-Li(2)	119.93(7)	C(11)-C(10)-Ni(1)	117.38(6)
C(11)-C(10)-Li(2)	114.96(7)	C(10)-C(11)-C(12)	115.63(7)
C(13)-C(12)-C(11)	113.64(8)	C(14)-C(13)-C(12)	124.68(9)
C(13)-C(14)-C(15)	124.74(9)	C(14)-C(15)-C(16)	112.50(8)
C(9)-C(16)-C(15)	114.25(8)	C(9)-C(16)-Li(1)	56.71(6)
C(15)-C(16)-Li(1)	150.30(8)	O(1)-C(17)-C(18)	105.75(7)
C(17)-C(18)-C(19)	102.41(7)	C(20)-C(19)-C(18)	101.04(7)
O(1)-C(20)-C(19)	105.71(7)	O(2)-C(21)-C(22A)	105.45(9)
O(2)-C(21)-C(22B)	104.6(2)	C(23)-C(22A)-C(21)	102.43(10)
C(23)-C(22B)-C(21)	103.2(4)	C(22A)-C(23)-C(24)	100.57(10)

C(22B)-C(23)-C(24)	109.1(3)	O(2)-C(24)-C(23)	105.78(8)
O(3)-C(25)-C(26)	106.38(8)	C(25)-C(26)-C(27)	103.68(9)
C(28)-C(27)-C(26)	101.28(10)	O(3)-C(28)-C(27)	104.89(9)
O(4)-C(29)-C(30)	105.63(8)	C(29)-C(30)-C(31)	101.26(9)
C(32)-C(31)-C(30)	102.47(8)	O(4)-C(32)-C(31)	105.83(8)
Ni(1)-Li(1)-C(16)	74.23(5)	O(1)-Li(1)-Ni(1)	131.95(8)
O(1)-Li(1)-O(2)	95.40(8)	O(1)-Li(1)-C(16)	88.68(7)
O(2)-Li(1)-Ni(1)	132.58(8)	O(2)-Li(1)-C(16)	109.84(8)
O(3)-Li(2)-Ni(1)	123.53(8)	O(3)-Li(2)-C(10)	106.00(8)
O(4)-Li(2)-Ni(1)	133.67(8)	O(4)-Li(2)-O(3)	101.77(8)
O(4)-Li(2)-C(10)	112.88(8)	C(10)-Li(2)-Ni(1)	49.44(4)

## Complex 22:



**Table 1. Crystal data and structure refinement.**

Identification code	11213
Empirical formula	$C_{16}H_{29}LiN_2Ni$
Color	colorless
Formula weight	$315.06 \text{ g} \cdot \text{mol}^{-1}$
Temperature	100(2) K
Wavelength	$0.71073 \text{ \AA}$
Crystal system	ORTHORHOMBIC
Space group	<b>Pbca, (no. 61)</b>
Unit cell dimensions	$a = 16.5550(13) \text{ \AA}$ $\alpha = 90^\circ$ . $b = 11.7095(2) \text{ \AA}$ $\beta = 90^\circ$ . $c = 17.7899(14) \text{ \AA}$ $\gamma = 90^\circ$ .
Volume	$3448.6(4) \text{ \AA}^3$

Z	8	
Density (calculated)	1.214 Mg · m <sup>-3</sup>	
Absorption coefficient	1.117 mm <sup>-1</sup>	
F(000)	1360 e	
Crystal size	0.16 x 0.13 x 0.08 mm <sup>3</sup>	
θ range for data collection	3.014 to 35.997°.	
Index ranges	-27 ≤ h ≤ 27, -19 ≤ k ≤ 19, -29 ≤ l ≤ 29	
Reflections collected	120298	
Independent reflections	8158 [R <sub>int</sub> = 0.0583]	
Reflections with I > 2σ(I)	6100	
Completeness to θ = 25.242°	99.6 %	
Absorption correction	Gaussian	
Max. and min. transmission	0.92 and 0.86	
Refinement method	Full-matrix least-squares on F <sup>2</sup>	
Data / restraints / parameters	8158 / 0 / 231	
Goodness-of-fit on F <sup>2</sup>	1.043	
Final R indices [I > 2σ(I)]	R <sub>1</sub> = 0.0389	wR <sup>2</sup> = 0.0902
R indices (all data)	R <sub>1</sub> = 0.0617	wR <sup>2</sup> = 0.1018
Largest diff. peak and hole	1.4 and -0.6 e · Å <sup>-3</sup>	



**Table 2. Bond lengths [Å] and angles [°].**

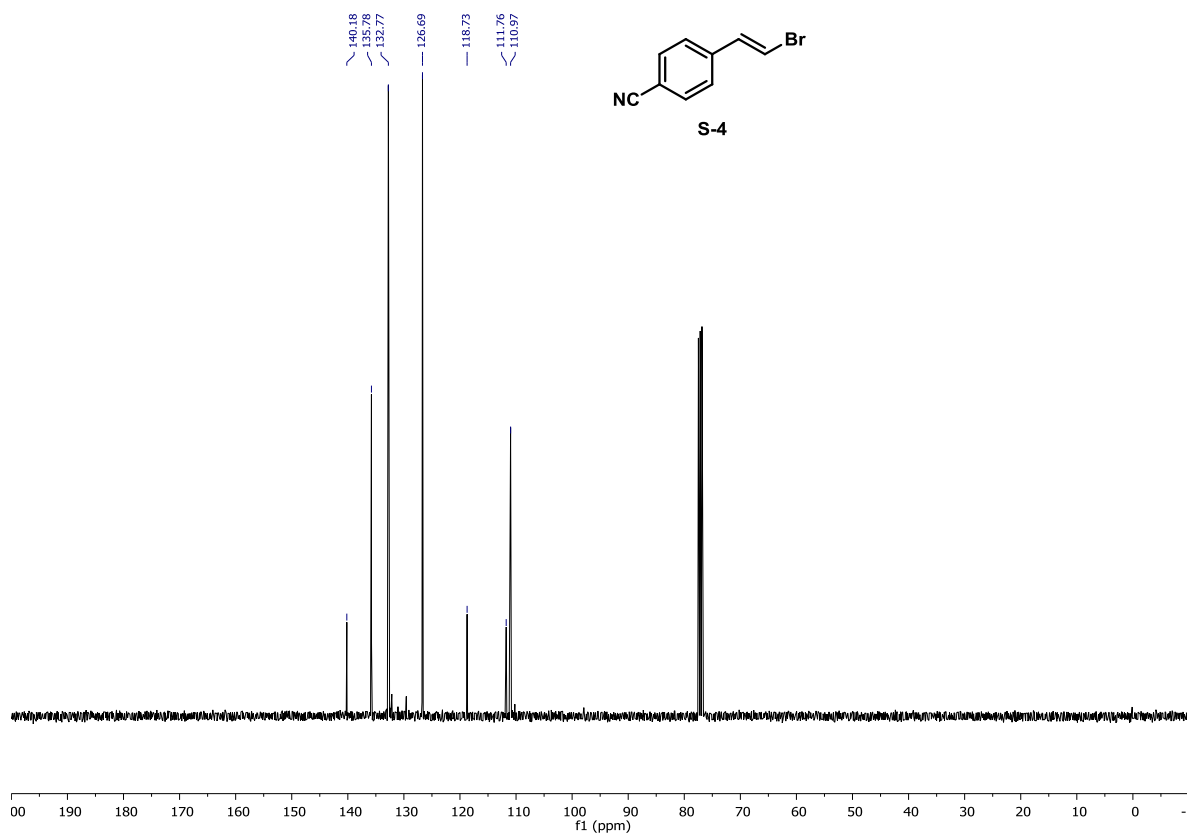
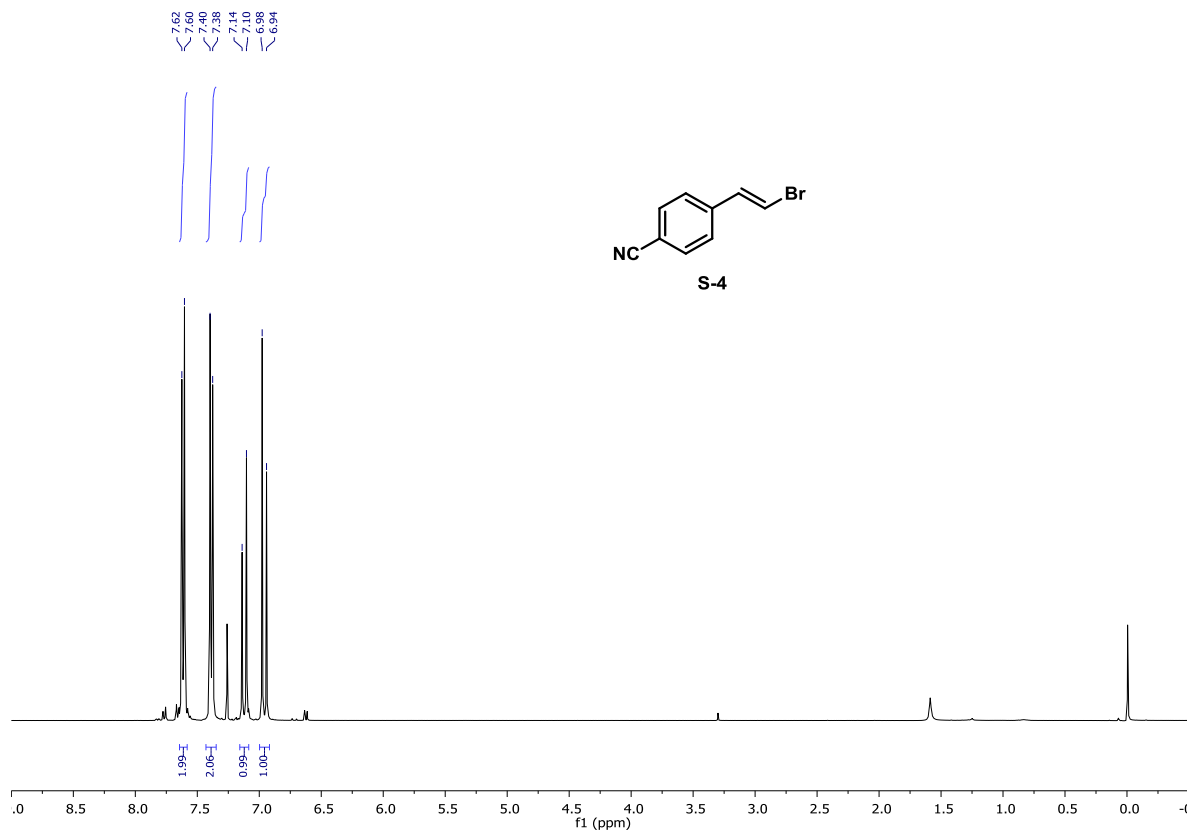
---

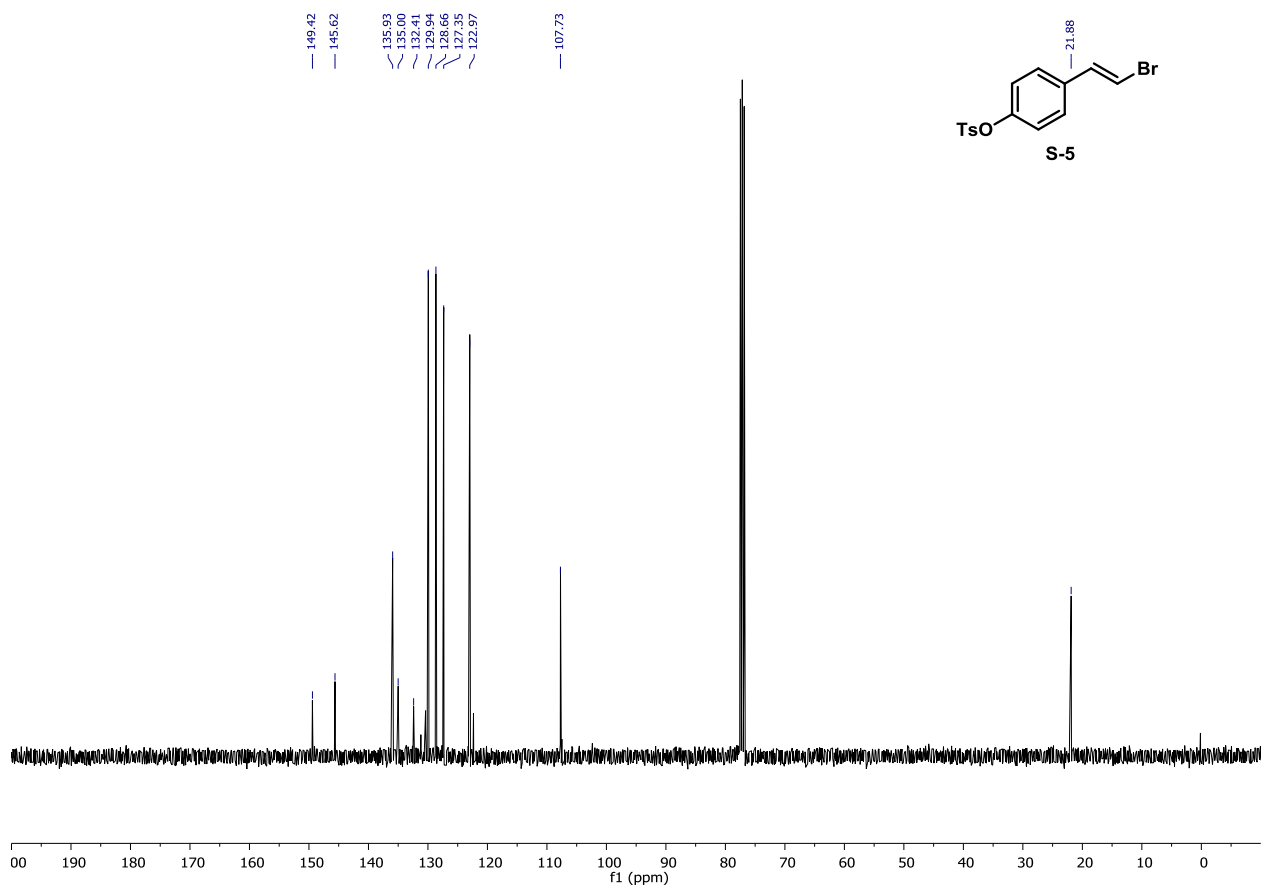
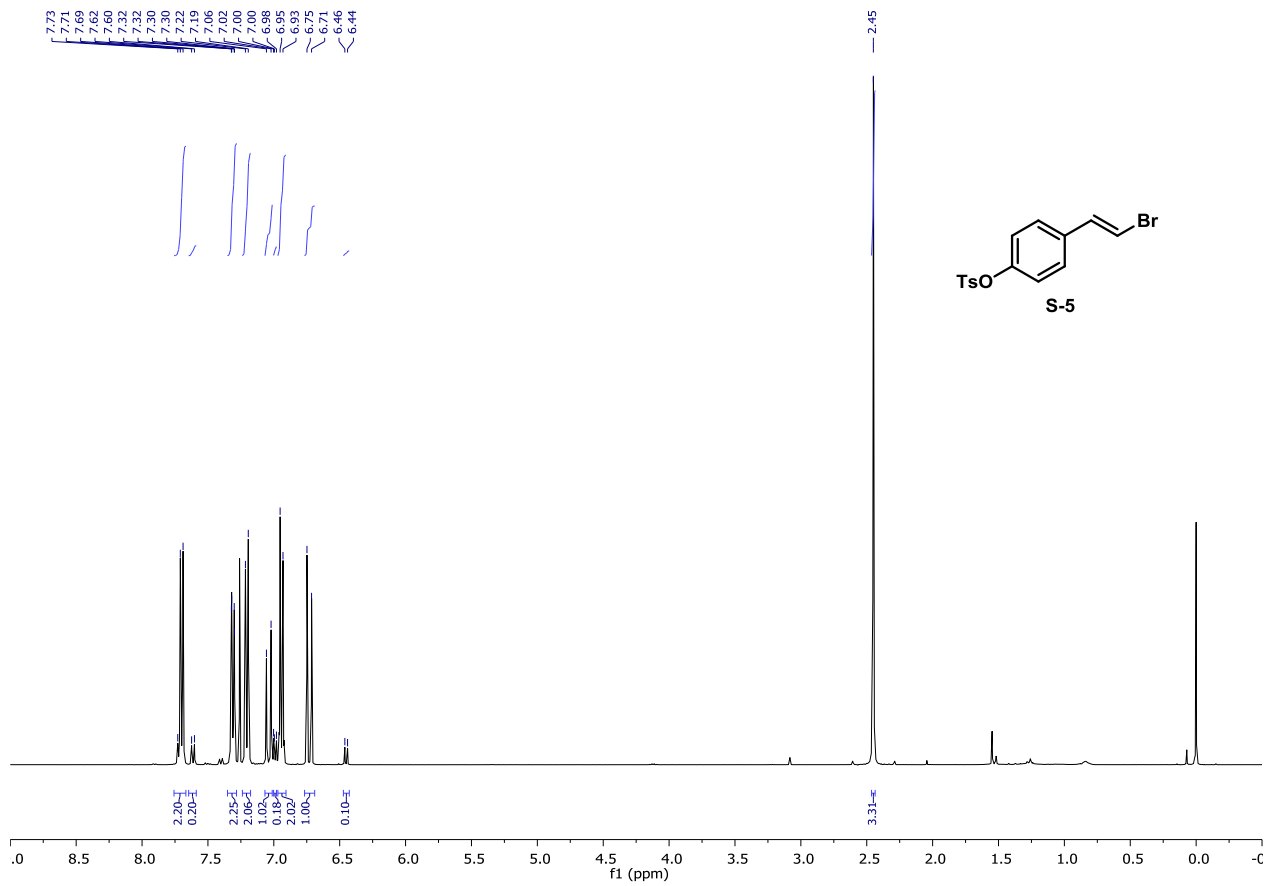
Ni(1)-C(7)	1.9815(14)	Ni(1)-C(8)	1.9665(14)
Ni(1)-C(9)	1.9869(14)	Ni(1)-C(10)	1.9788(15)
Ni(1)-C(11)	1.9634(12)	Ni(1)-Li(1)	2.500(2)
N(1)-C(1)	1.4990(19)	N(1)-C(3)	1.4616(19)
N(1)-C(4)	1.453(2)	N(1)-Li(1)	2.060(3)
N(2)-C(2)	1.4706(19)	N(2)-C(5)	1.478(2)
N(2)-C(6)	1.4683(19)	N(2)-Li(1)	2.076(3)
C(1)-H(1A)	1.06(2)	C(1)-H(1B)	1.05(2)
C(1)-C(2)	1.511(2)	C(2)-H(2A)	1.08(2)
C(2)-H(2B)	0.99(2)	C(7)-H(7A)	0.94(2)
C(7)-H(7B)	0.98(2)	C(7)-C(8)	1.411(2)
C(7)-Li(1)	2.419(3)	C(8)-H(8A)	0.96(2)
C(8)-H(8B)	0.97(2)	C(9)-H(9A)	0.96(2)
C(9)-H(9B)	0.98(2)	C(9)-C(10)	1.397(2)
C(10)-H(10A)	0.96(2)	C(10)-H(10B)	0.96(2)
C(11)-C(12)	1.4143(17)	C(11)-C(16)	1.4161(18)
C(11)-Li(1)	2.197(3)	C(12)-C(13)	1.4002(19)
C(12)-Li(1)	2.607(3)	C(13)-C(14)	1.385(2)
C(14)-C(15)	1.391(2)	C(15)-C(16)	1.3923(18)
Li(1)-H(7A)	2.09(2)		
C(7)-Ni(1)-C(9)	129.52(6)	C(7)-Ni(1)-Li(1)	64.12(7)
C(8)-Ni(1)-C(7)	41.87(6)	C(8)-Ni(1)-C(9)	87.87(7)
C(8)-Ni(1)-C(10)	128.97(6)	C(8)-Ni(1)-Li(1)	98.48(7)
C(9)-Ni(1)-Li(1)	140.19(7)	C(10)-Ni(1)-C(7)	170.79(6)
C(10)-Ni(1)-C(9)	41.27(6)	C(10)-Ni(1)-Li(1)	122.19(7)
C(11)-Ni(1)-C(7)	99.14(5)	C(11)-Ni(1)-C(8)	140.31(6)
C(11)-Ni(1)-C(9)	131.31(6)	C(11)-Ni(1)-C(10)	90.07(5)
C(11)-Ni(1)-Li(1)	57.46(7)	C(1)-N(1)-Li(1)	101.51(11)
C(3)-N(1)-C(1)	107.55(12)	C(3)-N(1)-Li(1)	117.74(12)
C(4)-N(1)-C(1)	112.05(13)	C(4)-N(1)-C(3)	109.24(12)
C(4)-N(1)-Li(1)	108.60(12)	C(2)-N(2)-C(5)	108.63(13)

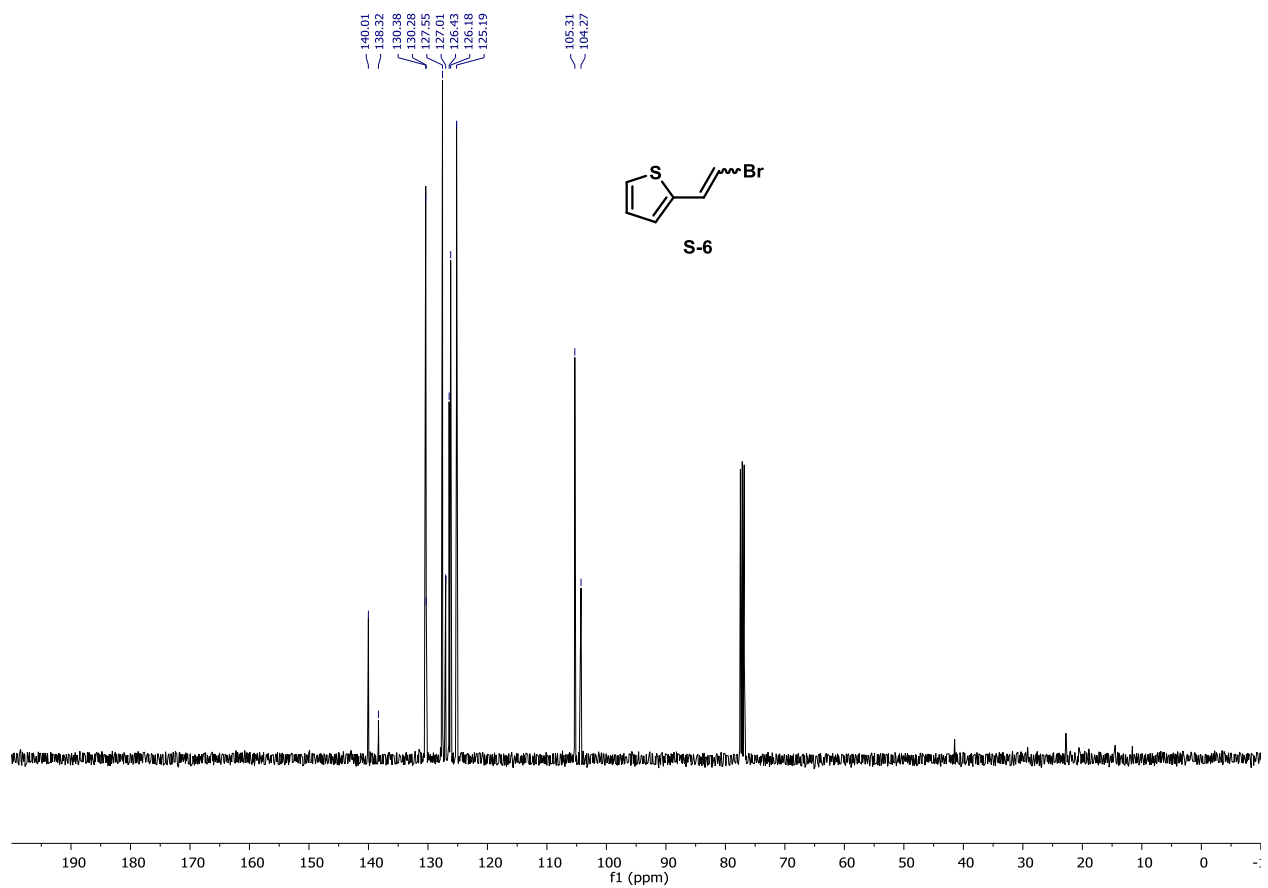
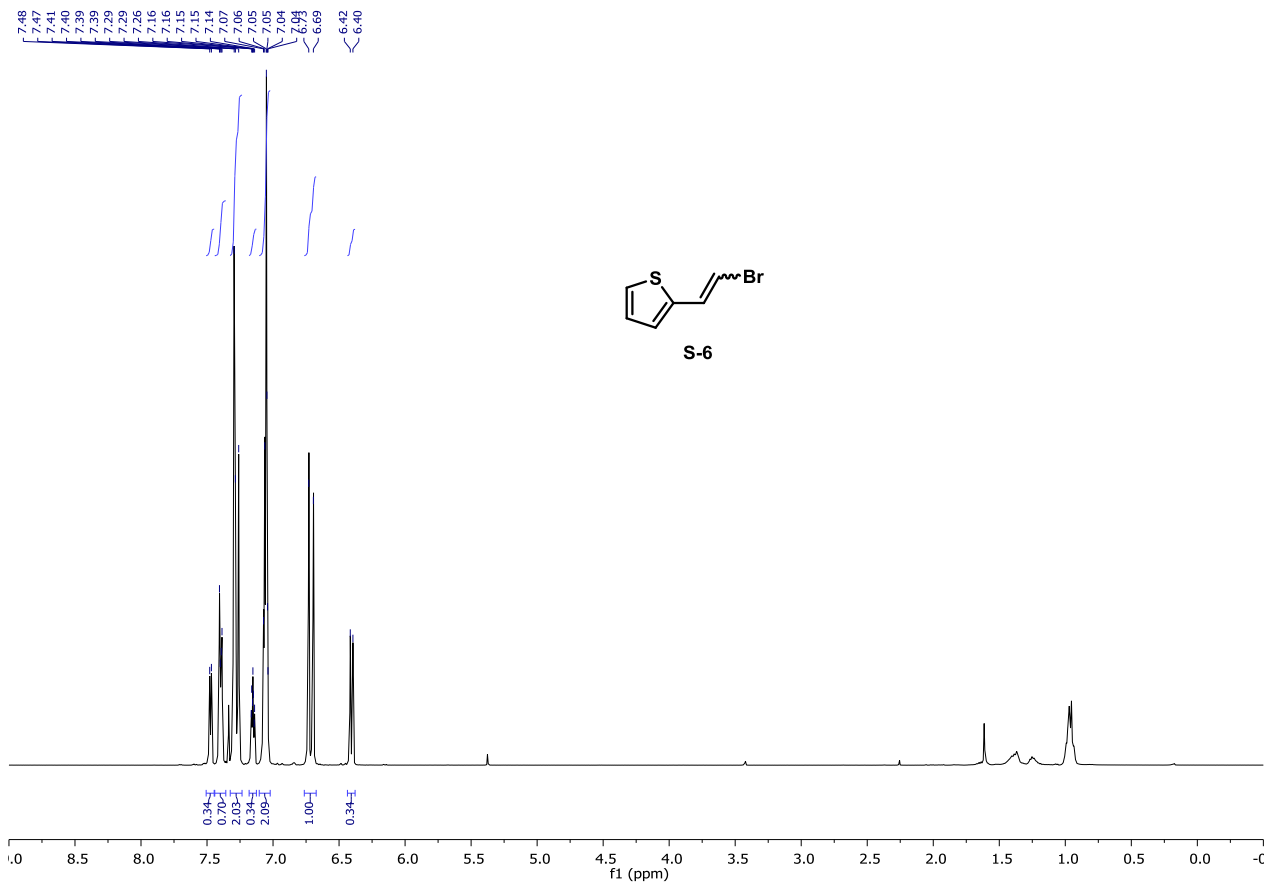
C(2)-N(2)-Li(1)	102.76(11)	C(5)-N(2)-Li(1)	115.49(12)
C(6)-N(2)-C(2)	112.24(12)	C(6)-N(2)-C(5)	107.91(12)
C(6)-N(2)-Li(1)	109.85(11)	N(1)-C(1)-H(1A)	109.7(12)
N(1)-C(1)-H(1B)	106.2(11)	N(1)-C(1)-C(2)	111.42(12)
H(1A)-C(1)-H(1B)	117.8(16)	C(2)-C(1)-H(1A)	104.4(12)
C(2)-C(1)-H(1B)	107.4(12)	N(2)-C(2)-C(1)	111.25(13)
N(2)-C(2)-H(2A)	107.1(12)	N(2)-C(2)-H(2B)	113.2(12)
C(1)-C(2)-H(2A)	110.0(11)	C(1)-C(2)-H(2B)	106.3(13)
H(2A)-C(2)-H(2B)	109.1(16)	N(1)-C(3)-H(3A)	117.8(13)
Ni(1)-C(7)-H(7B)	112.3(13)	Ni(1)-C(7)-Li(1)	68.41(7)
H(7A)-C(7)-H(7B)	116.0(18)	C(8)-C(7)-Ni(1)	68.50(8)
C(8)-C(7)-H(7A)	116.0(12)	C(8)-C(7)-H(7B)	117.7(12)
C(8)-C(7)-Li(1)	123.09(12)	Li(1)-C(7)-H(7A)	58.7(12)
Li(1)-C(7)-H(7B)	112.0(12)	Ni(1)-C(8)-H(8A)	112.7(13)
Ni(1)-C(8)-H(8B)	112.2(12)	C(7)-C(8)-Ni(1)	69.63(8)
C(7)-C(8)-H(8A)	122.7(14)	C(7)-C(8)-H(8B)	119.9(12)
H(8A)-C(8)-H(8B)	111.6(18)	Ni(1)-C(9)-H(9A)	110.6(14)
Ni(1)-C(9)-H(9B)	109.2(12)	H(9A)-C(9)-H(9B)	114.7(18)
C(10)-C(9)-Ni(1)	69.06(8)	C(10)-C(9)-H(9A)	120.3(14)
C(10)-C(9)-H(9B)	121.4(12)	Ni(1)-C(10)-H(10A)	111.3(11)
Ni(1)-C(10)-H(10B)	110.6(13)	C(9)-C(10)-Ni(1)	69.68(9)
C(9)-C(10)-H(10A)	121.1(11)	C(9)-C(10)-H(10B)	119.8(13)
H(10A)-C(10)-H(10B)	114.3(17)	Ni(1)-C(11)-Li(1)	73.65(7)
C(12)-C(11)-Ni(1)	126.98(9)	C(12)-C(11)-C(16)	114.14(11)
C(12)-C(11)-Li(1)	89.75(10)	C(16)-C(11)-Ni(1)	118.73(9)
C(16)-C(11)-Li(1)	113.11(11)	C(11)-C(12)-Li(1)	57.40(8)
C(13)-C(12)-C(11)	123.30(12)	C(13)-C(12)-Li(1)	126.50(11)
C(14)-C(13)-C(12)	120.09(13)	C(13)-C(14)-C(15)	118.84(12)
C(14)-C(15)-C(16)	120.48(13)	C(15)-C(16)-C(11)	123.08(12)
Ni(1)-Li(1)-H(7A)	67.2(6)	Ni(1)-Li(1)-C(12)	72.81(7)
N(1)-Li(1)-Ni(1)	161.33(13)	N(1)-Li(1)-N(2)	89.43(10)
N(1)-Li(1)-C(7)	116.51(12)	N(1)-Li(1)-H(7A)	99.9(6)
N(1)-Li(1)-C(11)	127.49(13)	N(1)-Li(1)-C(12)	113.50(11)
N(2)-Li(1)-Ni(1)	105.60(10)	N(2)-Li(1)-C(7)	113.59(11)
N(2)-Li(1)-H(7A)	99.8(6)	N(2)-Li(1)-C(11)	130.64(13)
N(2)-Li(1)-C(12)	108.16(11)	C(7)-Li(1)-Ni(1)	47.47(6)

C(7)-Li(1)-H(7A)	22.7(6)	C(7)-Li(1)-C(12)	113.19(10)
C(11)-Li(1)-Ni(1)	48.89(6)	C(11)-Li(1)-C(7)	81.00(9)
C(11)-Li(1)-H(7A)	103.6(6)	C(11)-Li(1)-C(12)	32.85(5)
C(12)-Li(1)-H(7A)	135.9(6)		

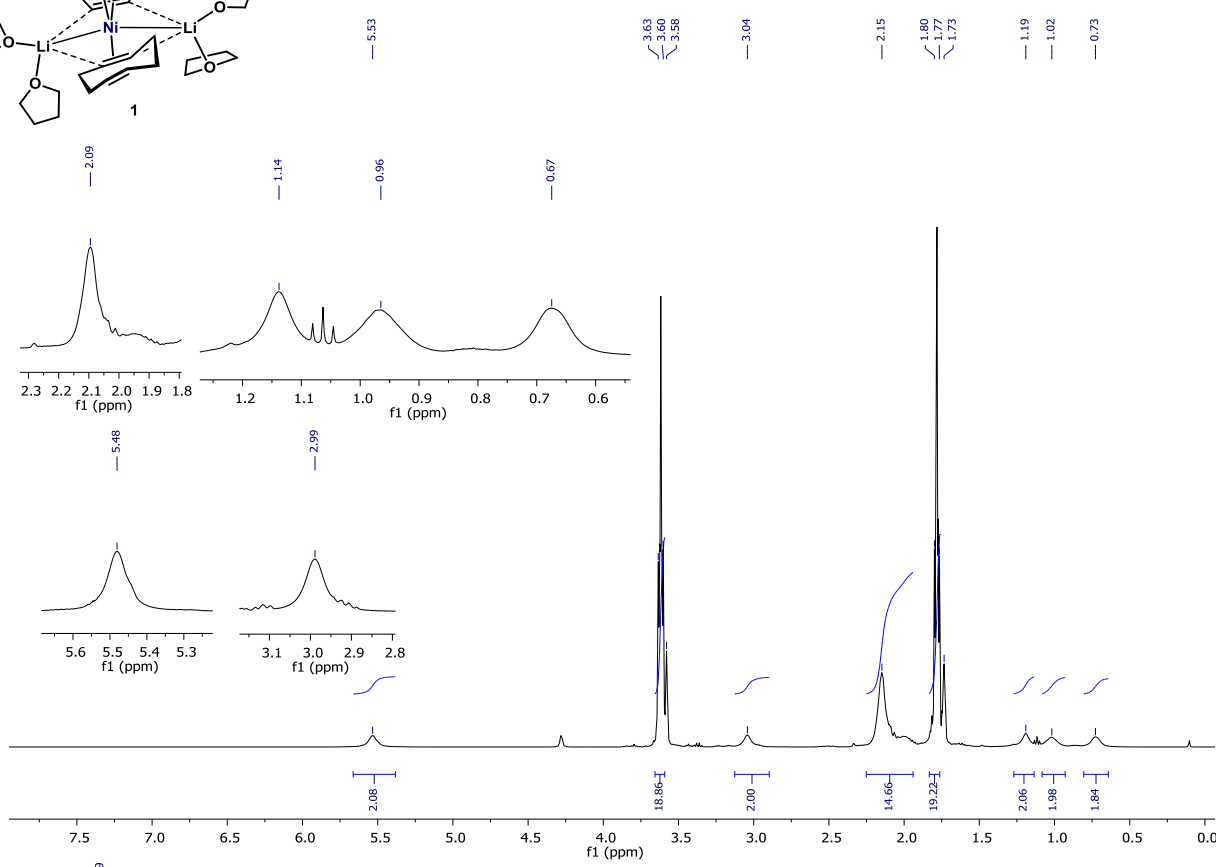
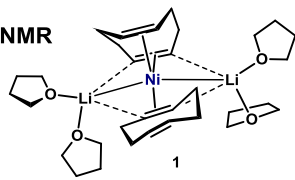
# 13 NMR Spectra



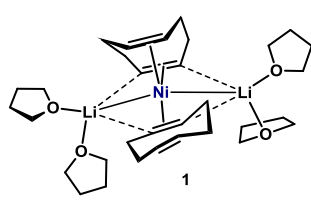
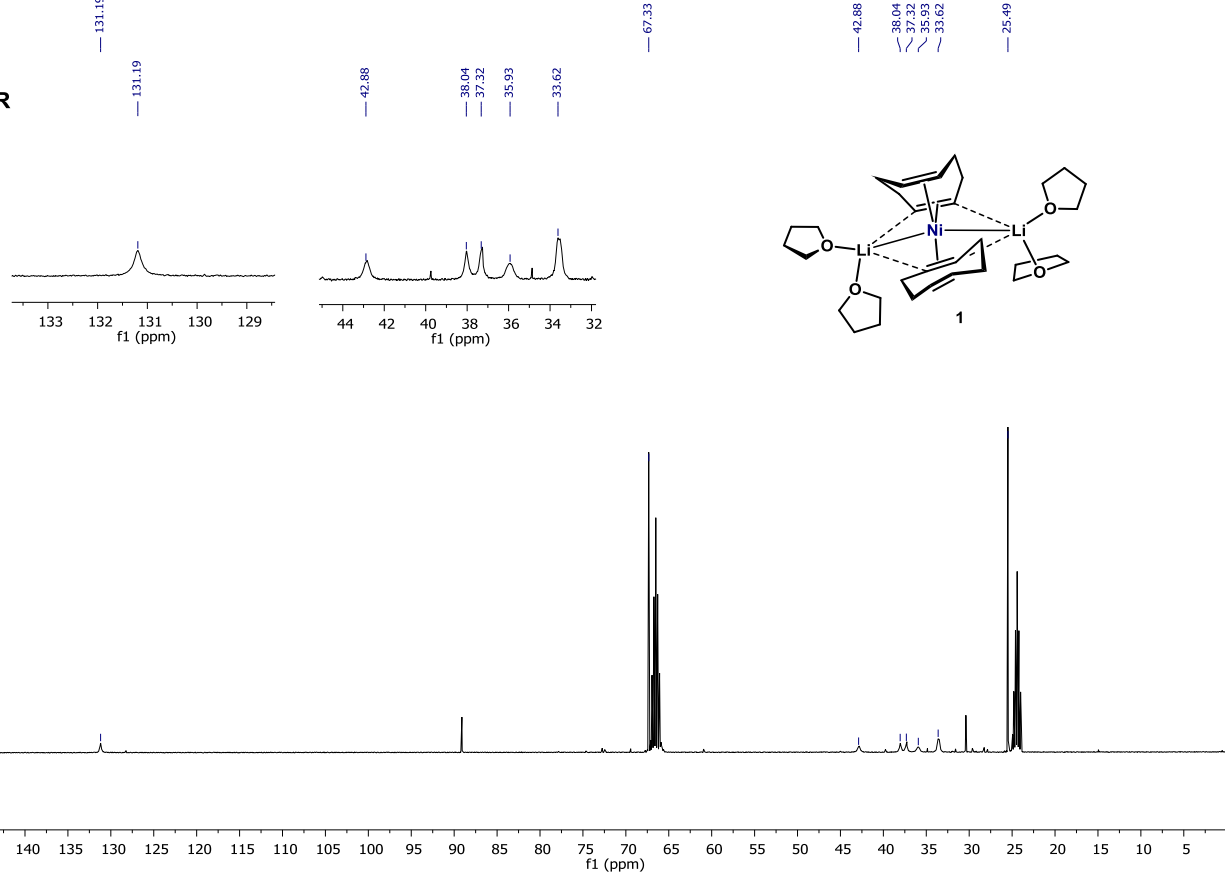




**<sup>1</sup>H NMR**

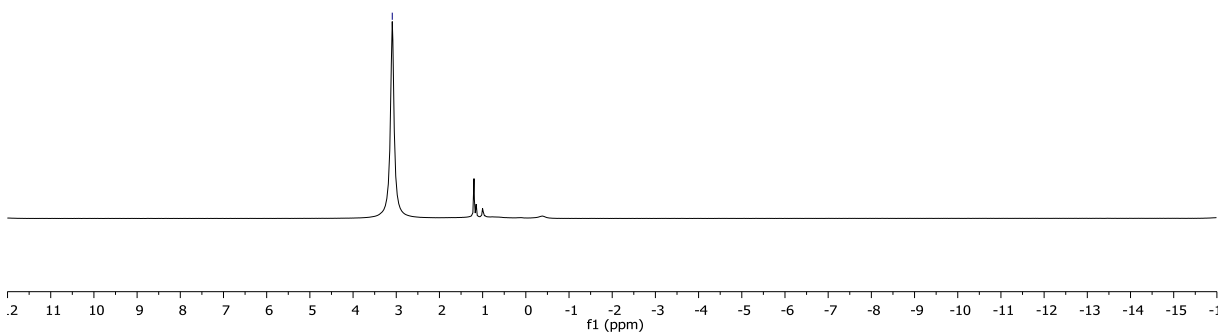
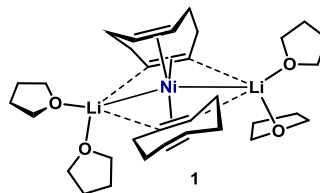


**<sup>13</sup>C NMR**

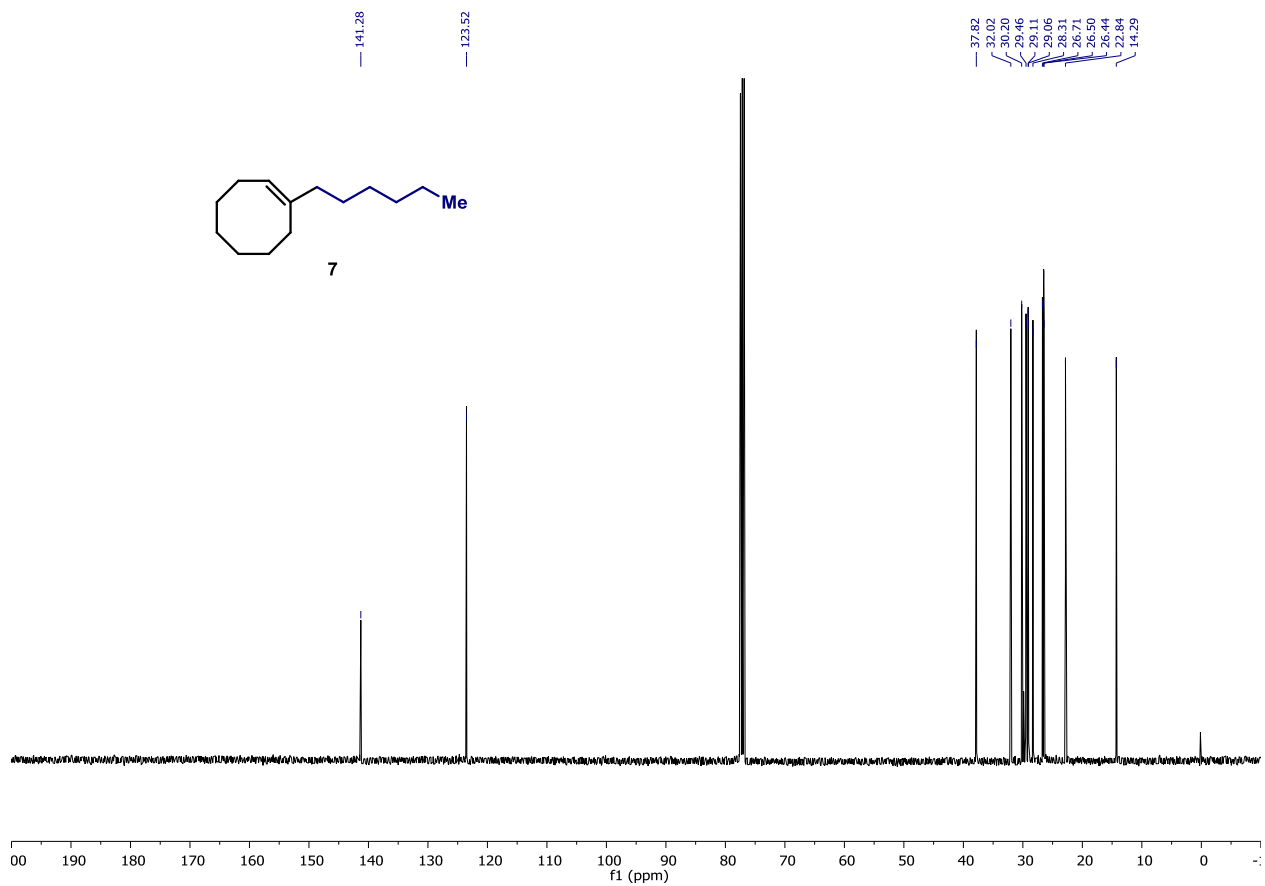
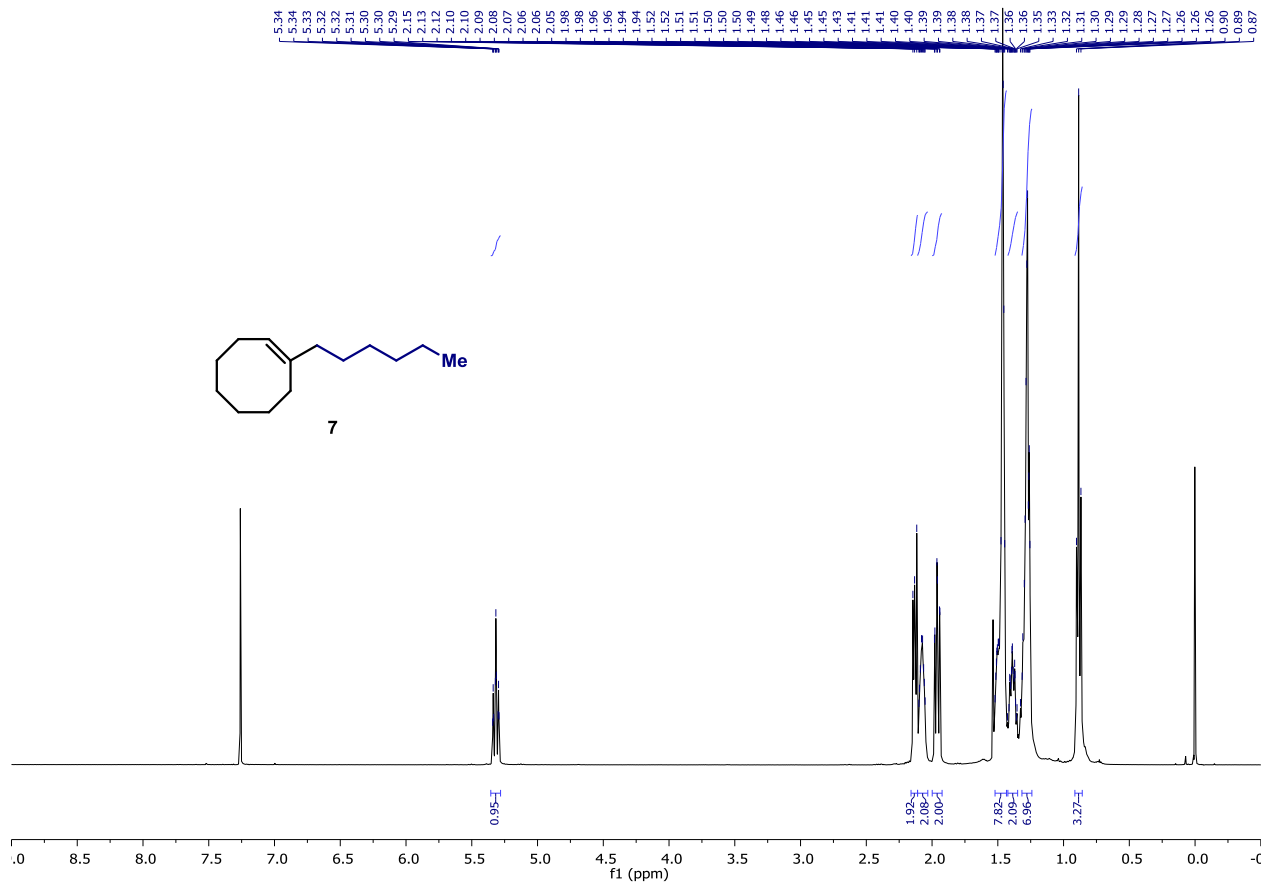


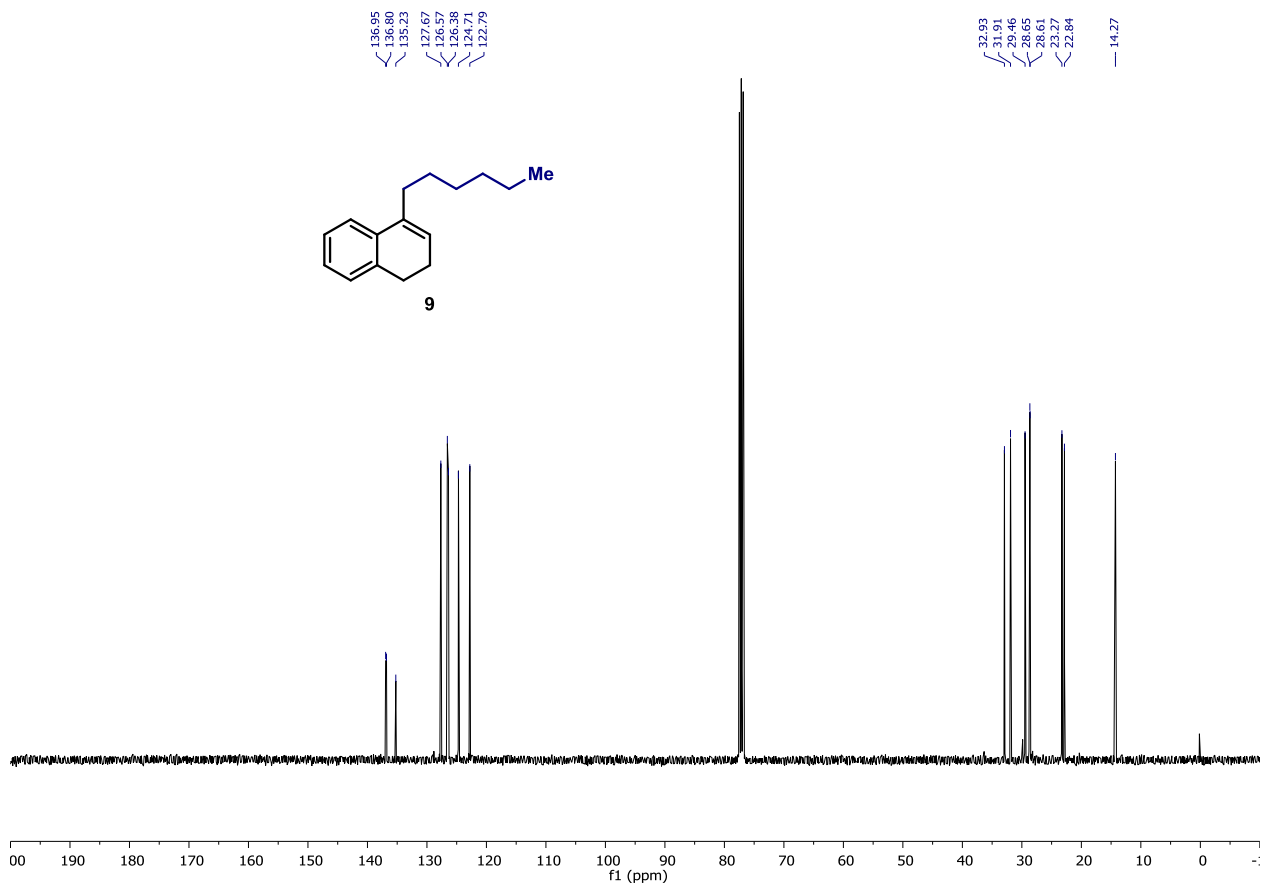
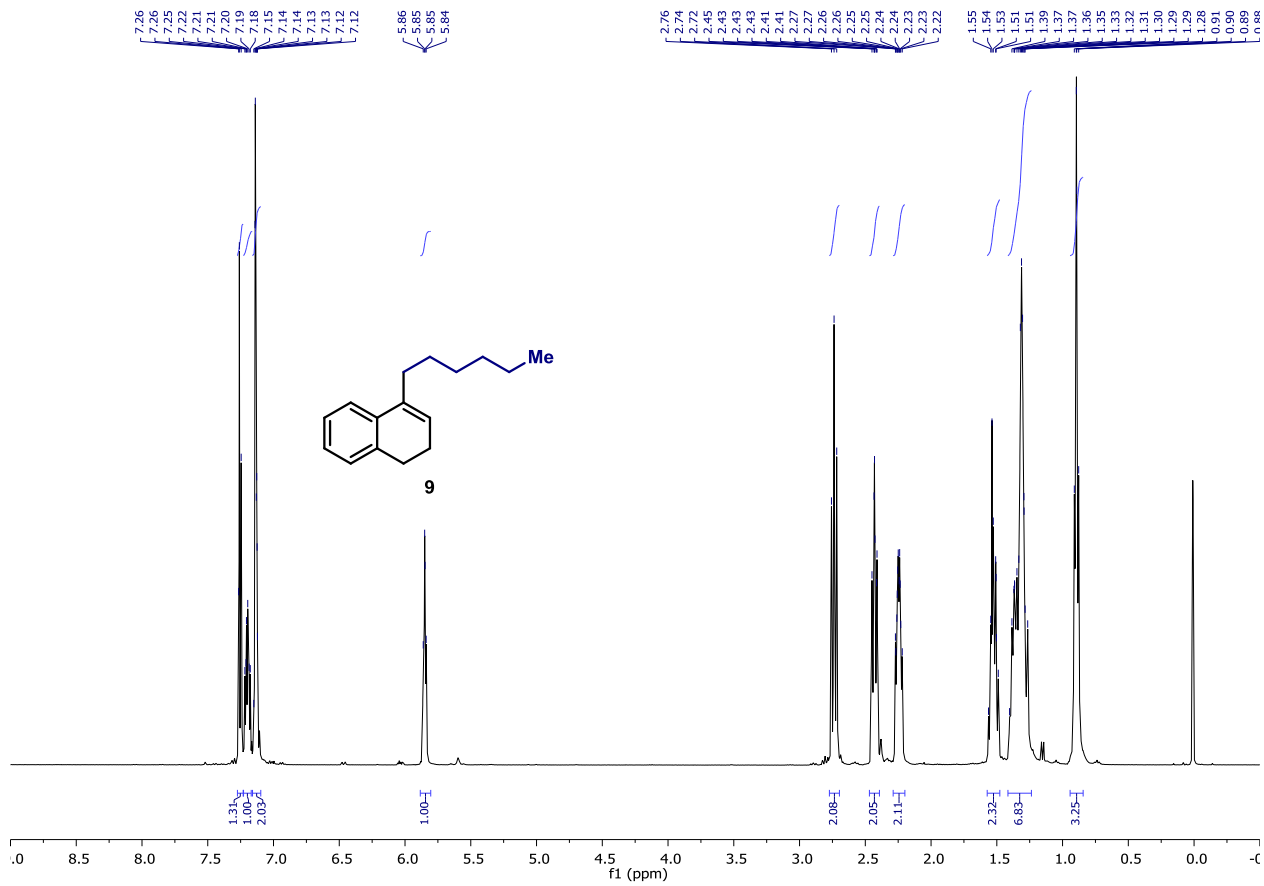
$^7\text{Li}$  NMR

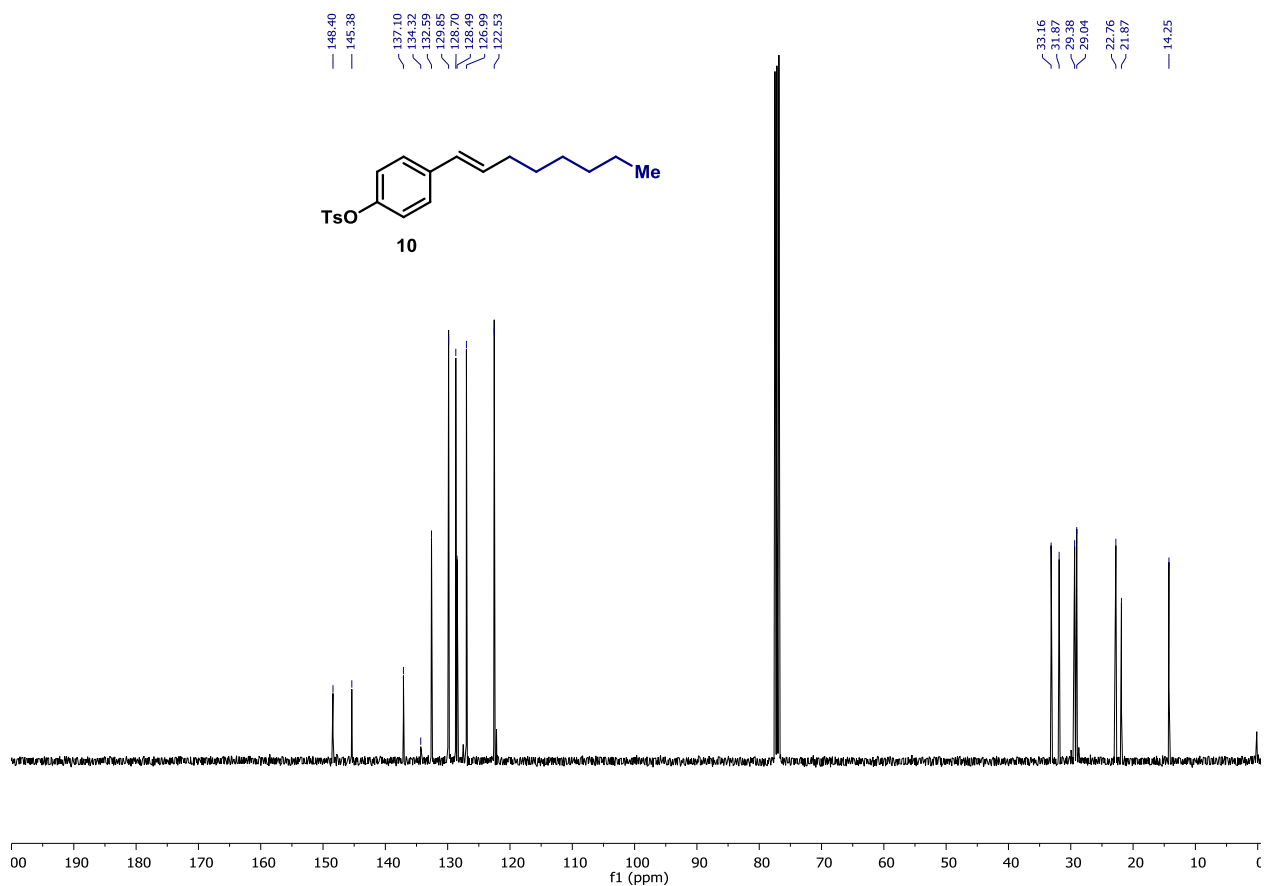
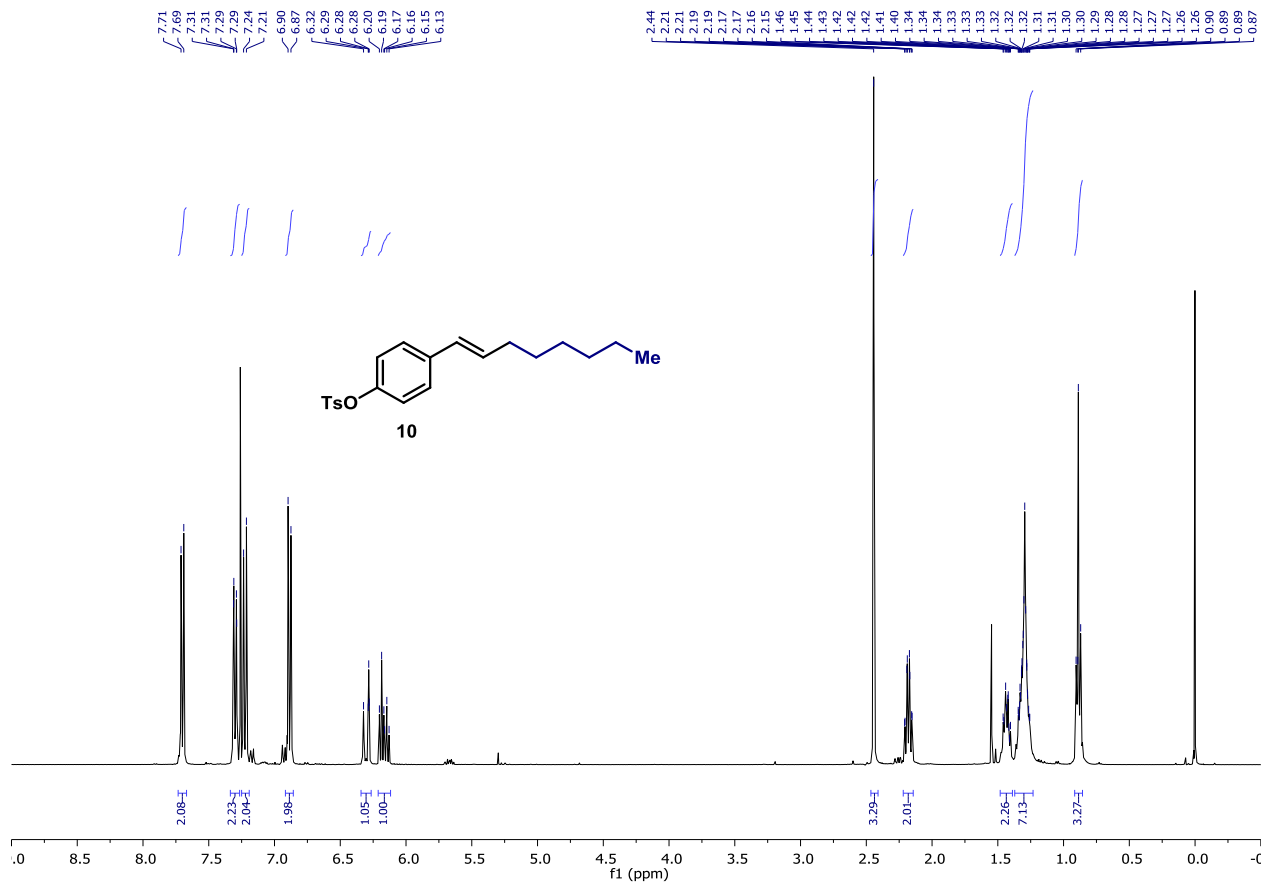
— 3.09

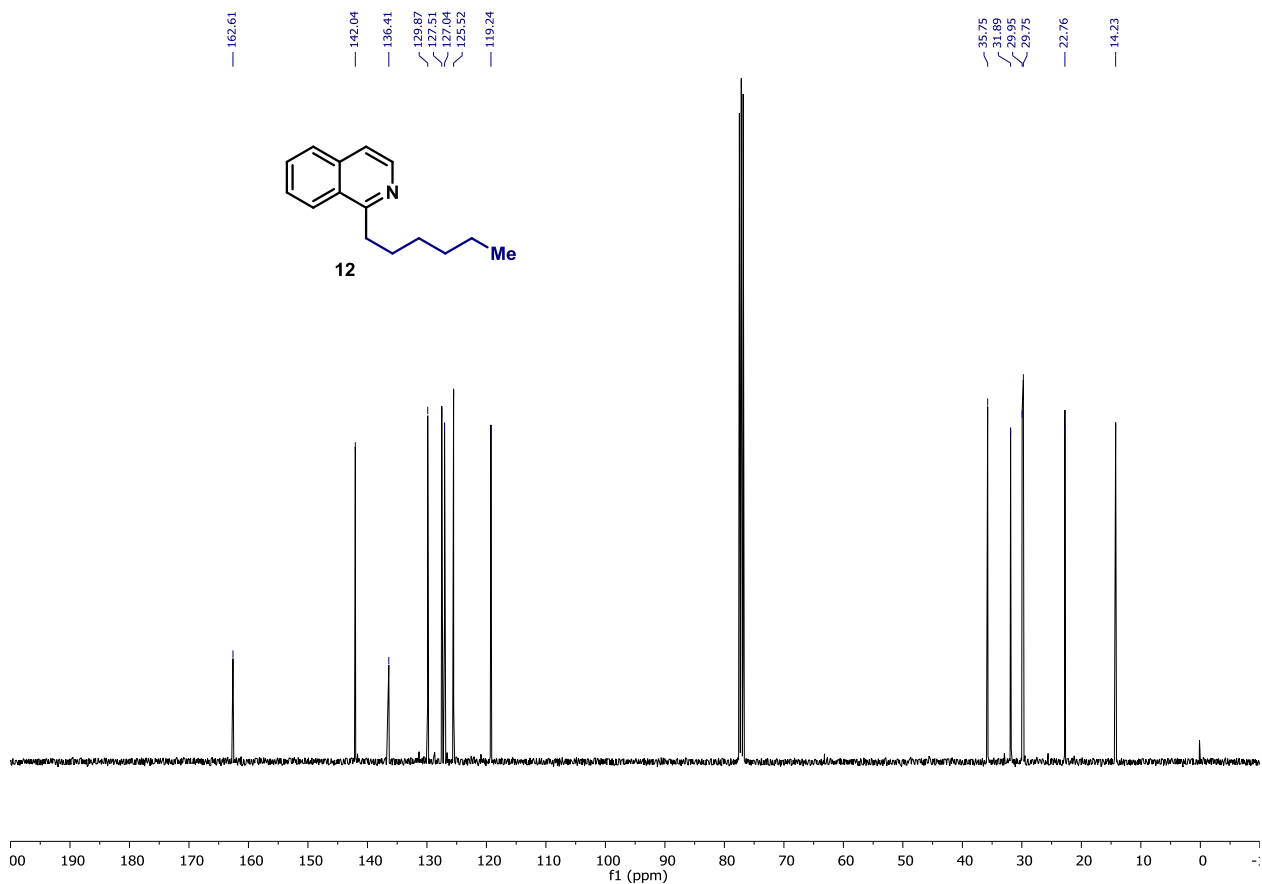
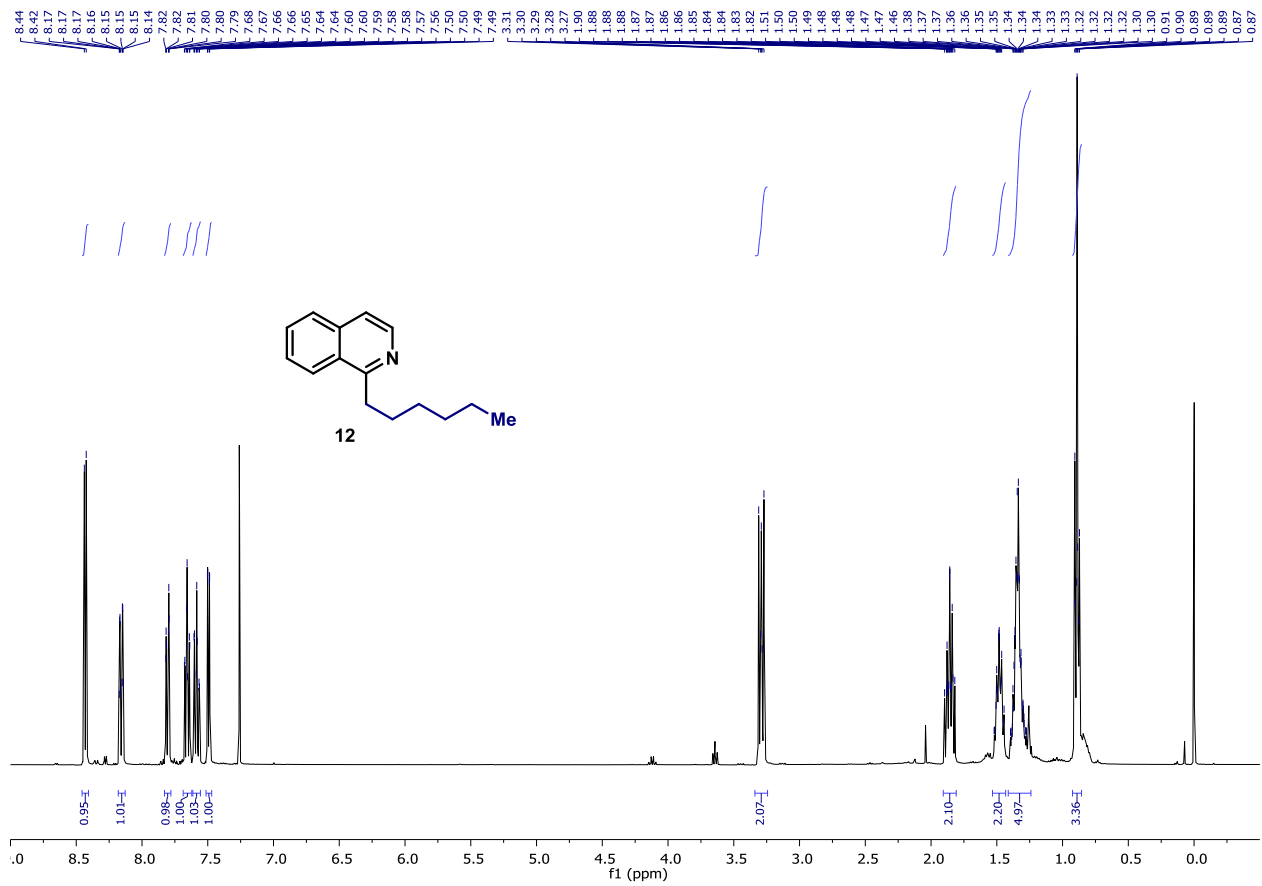




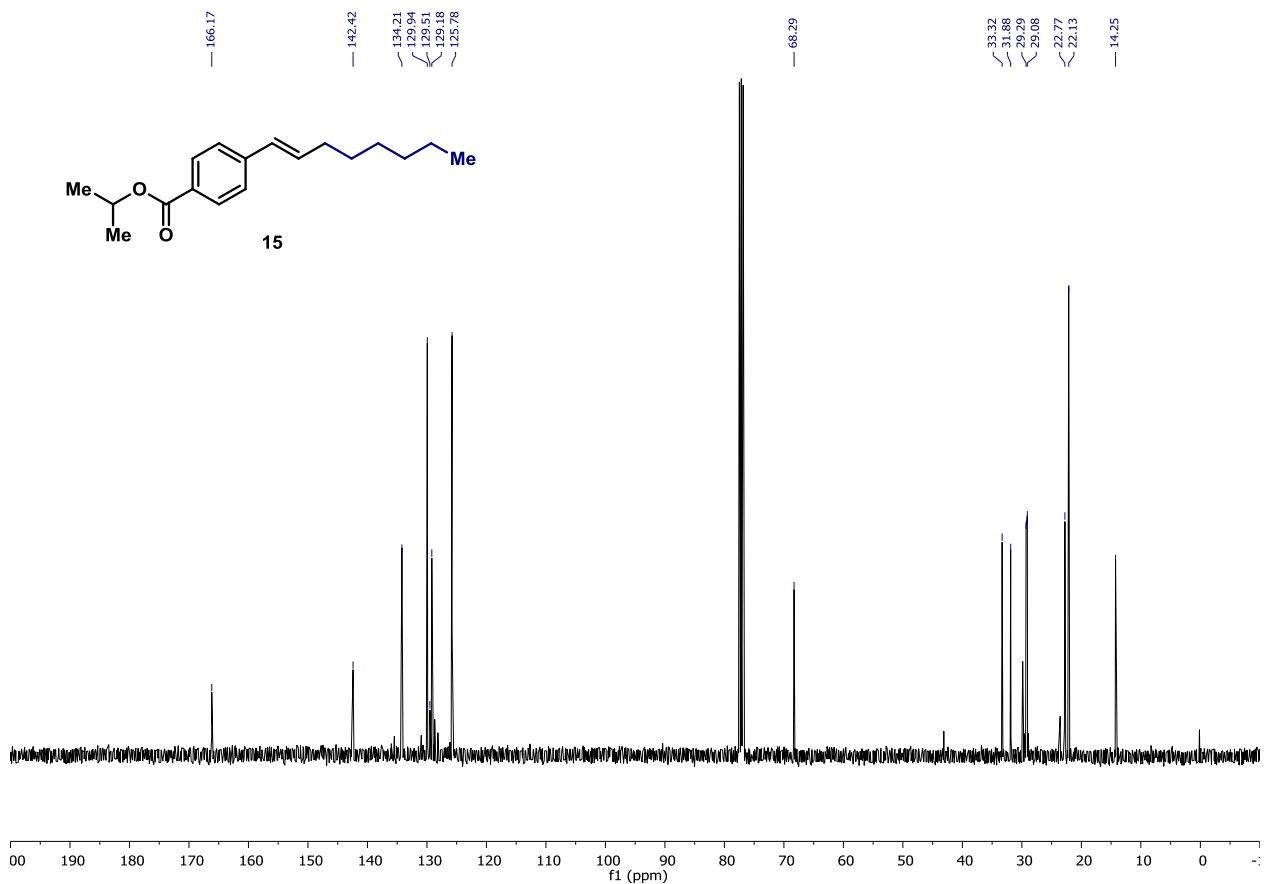
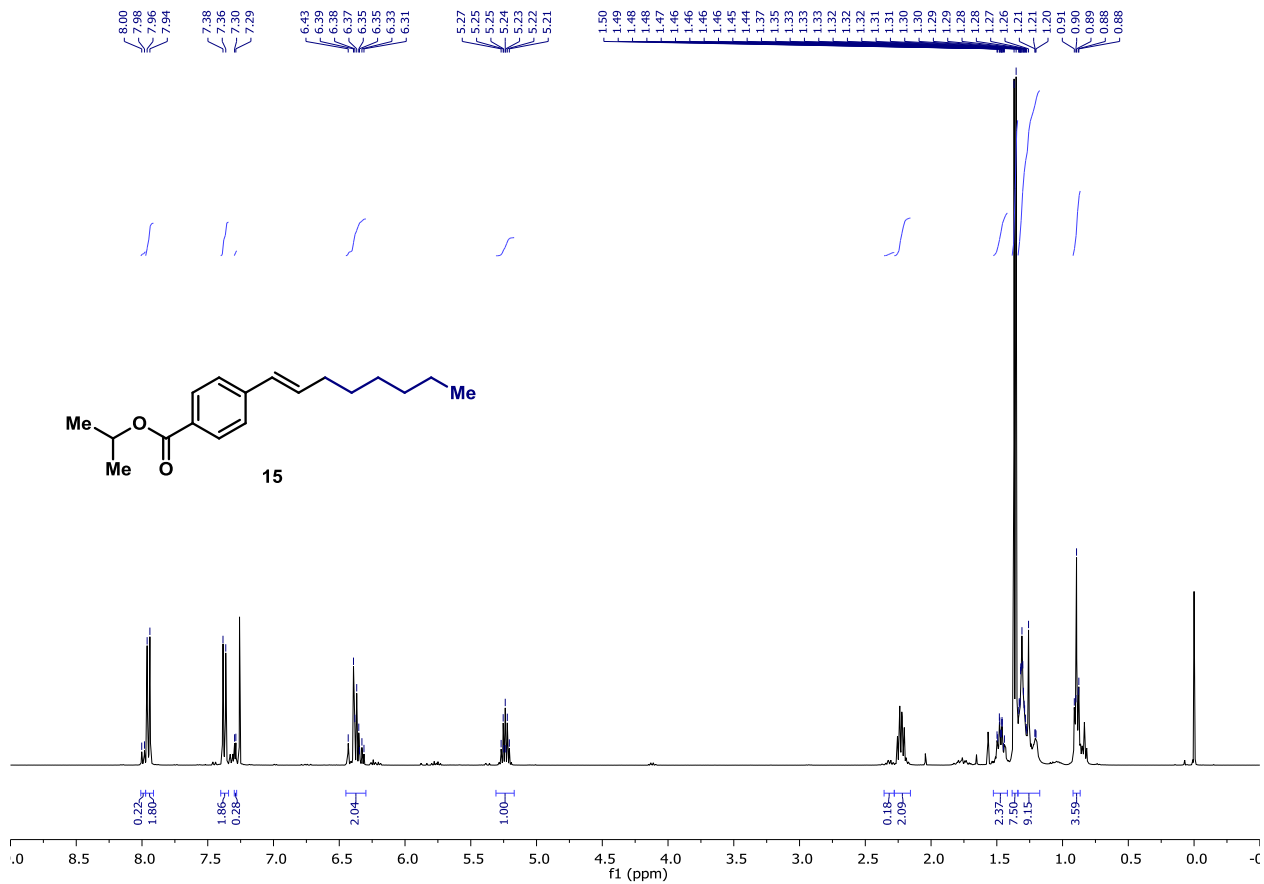


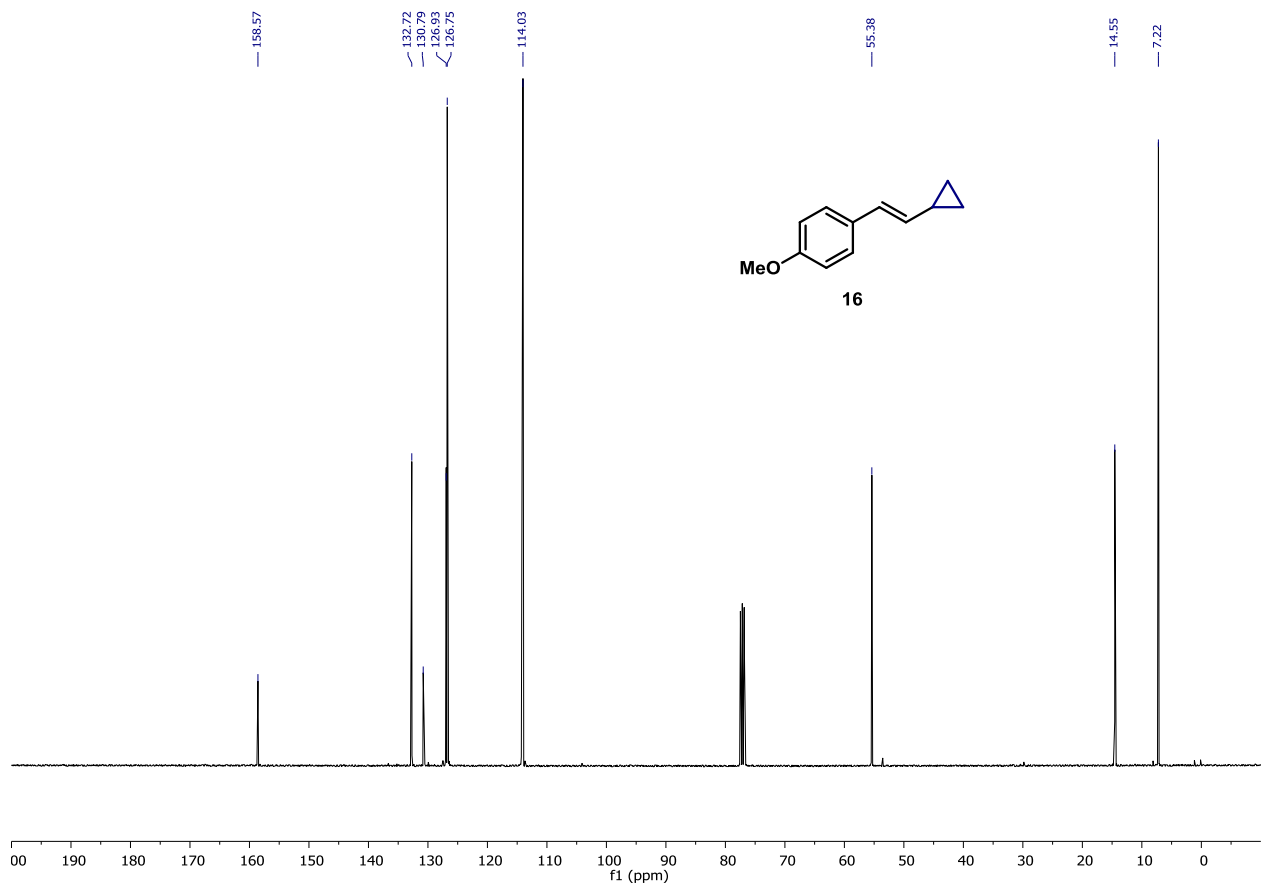
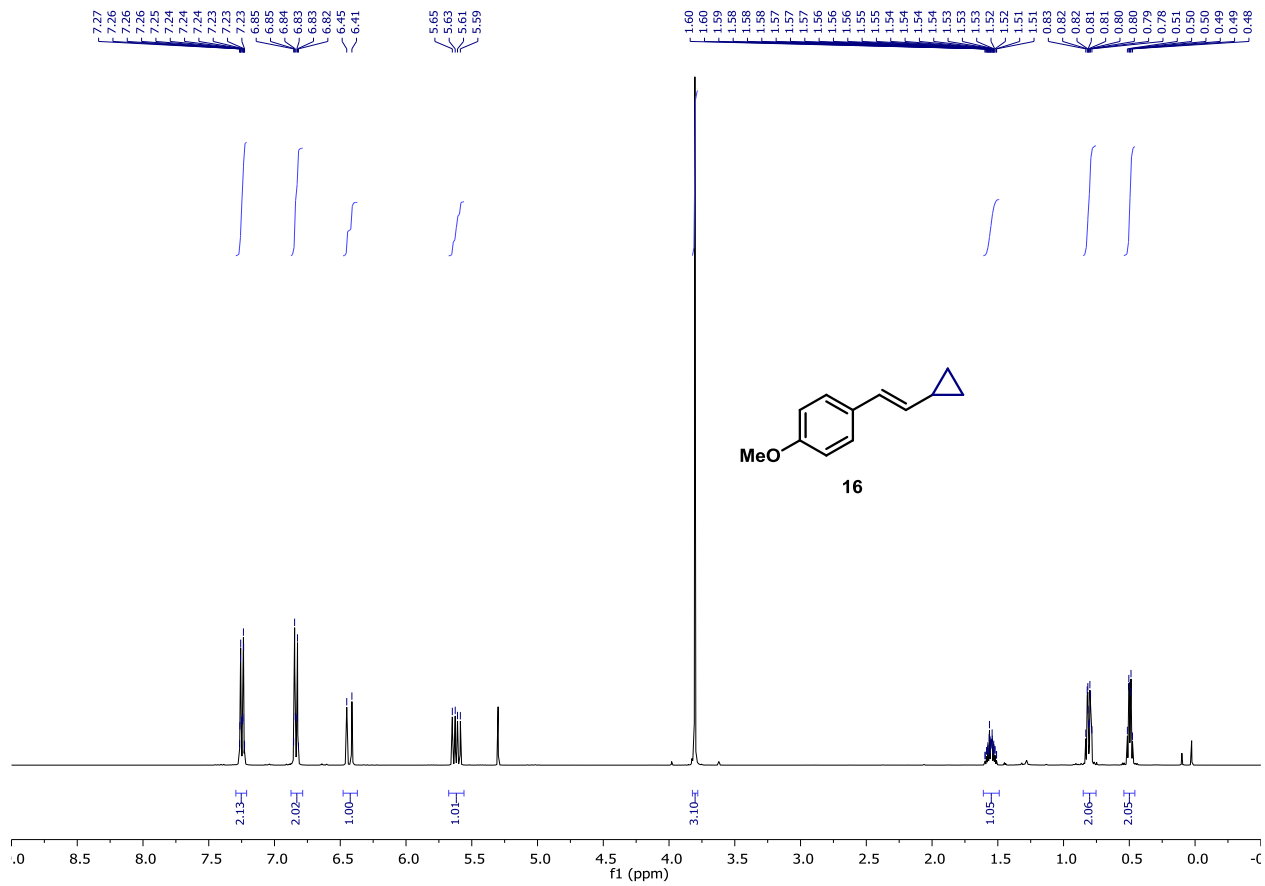


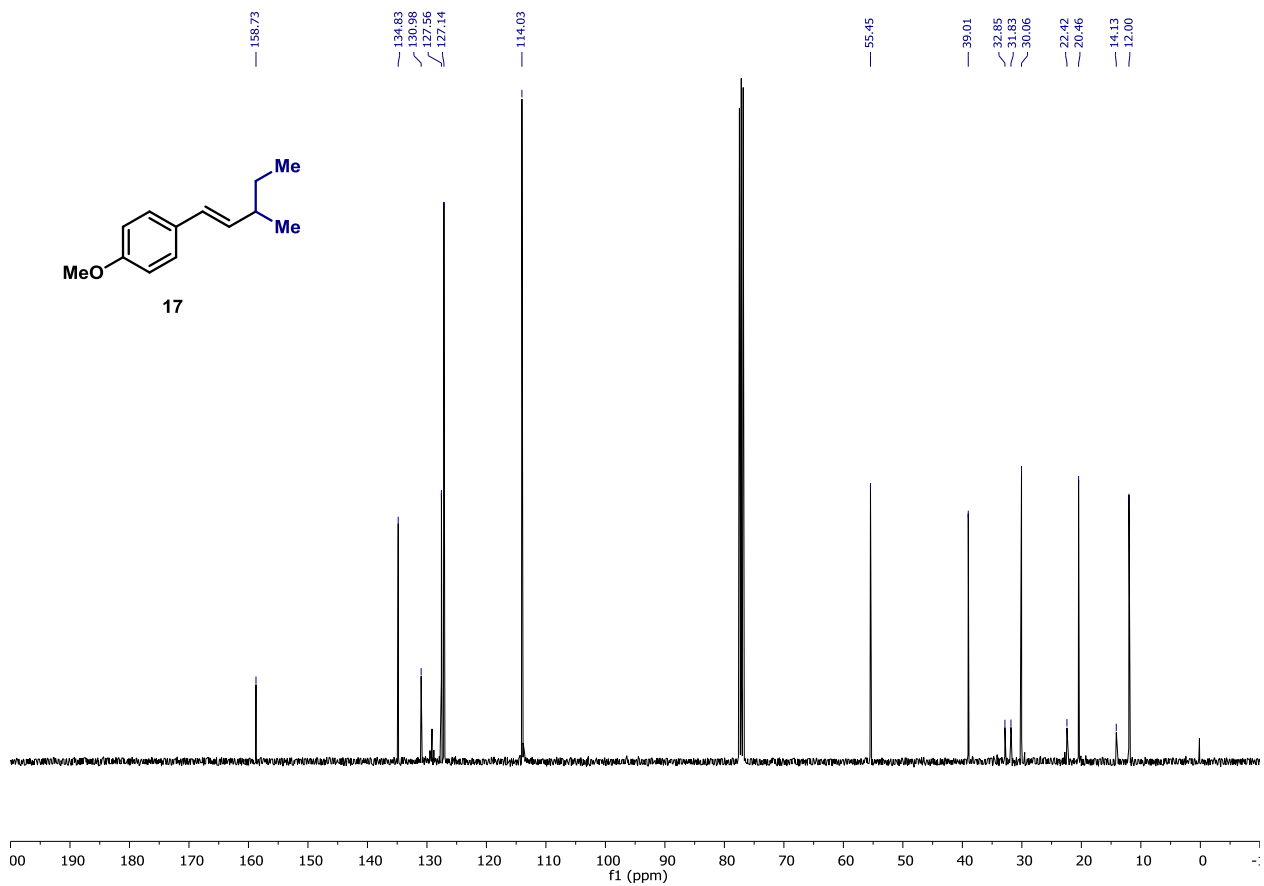
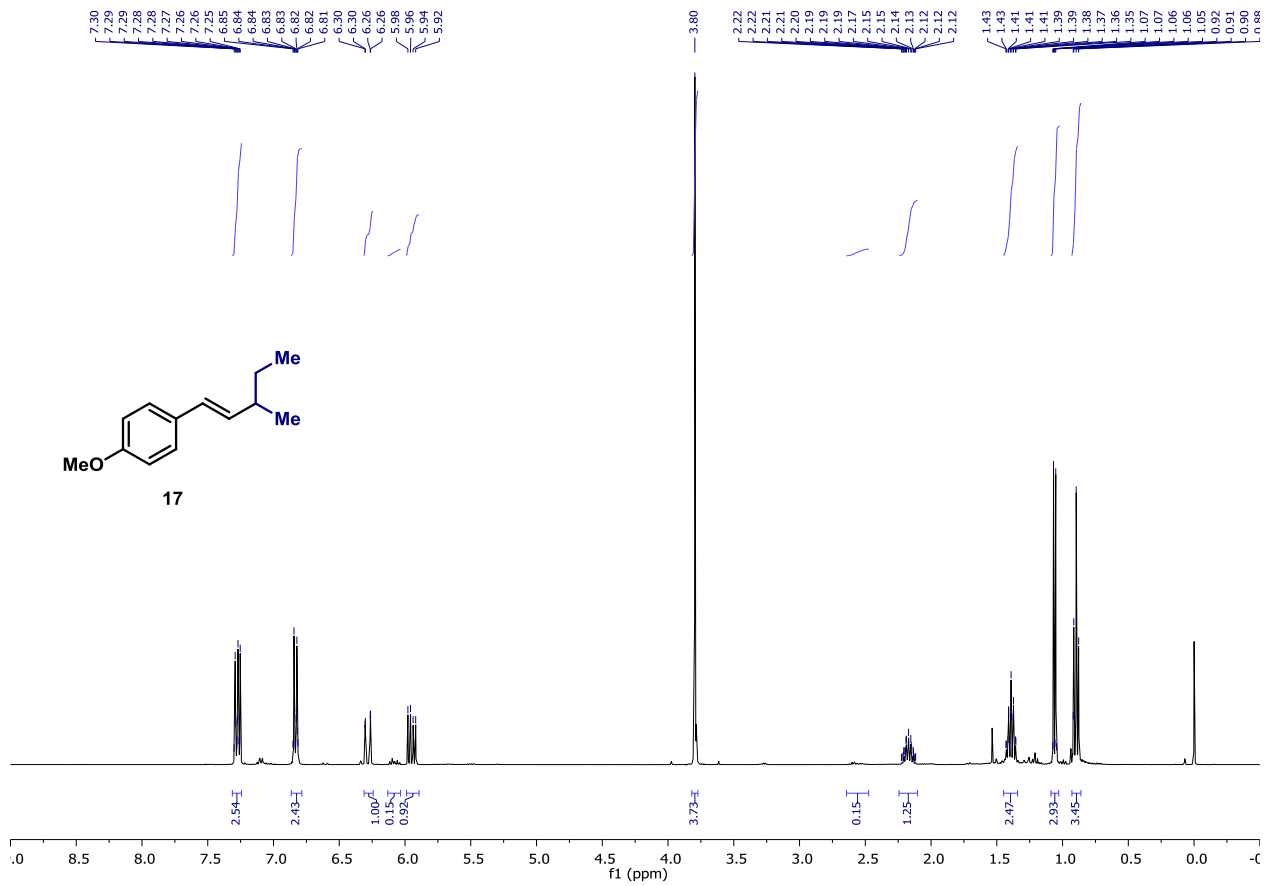






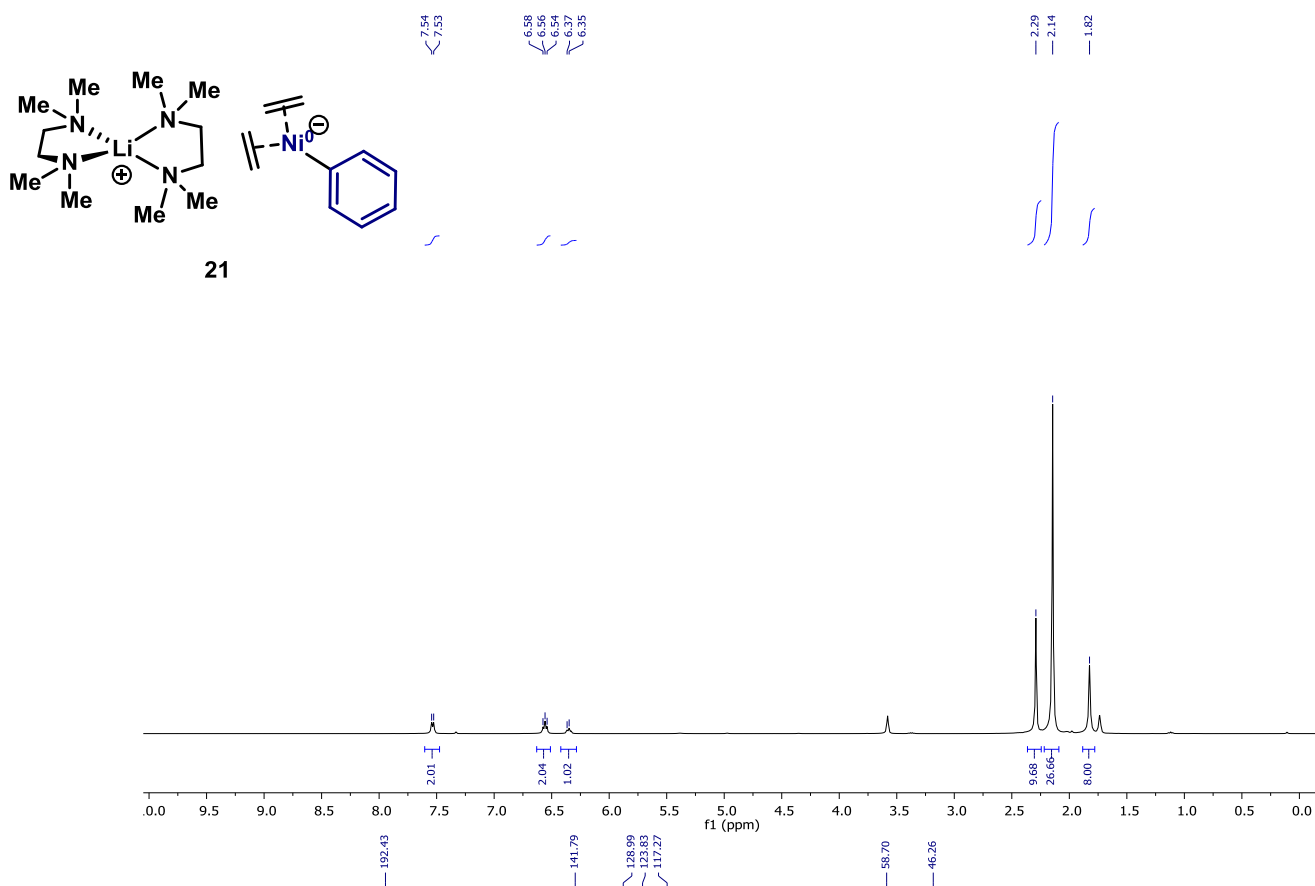




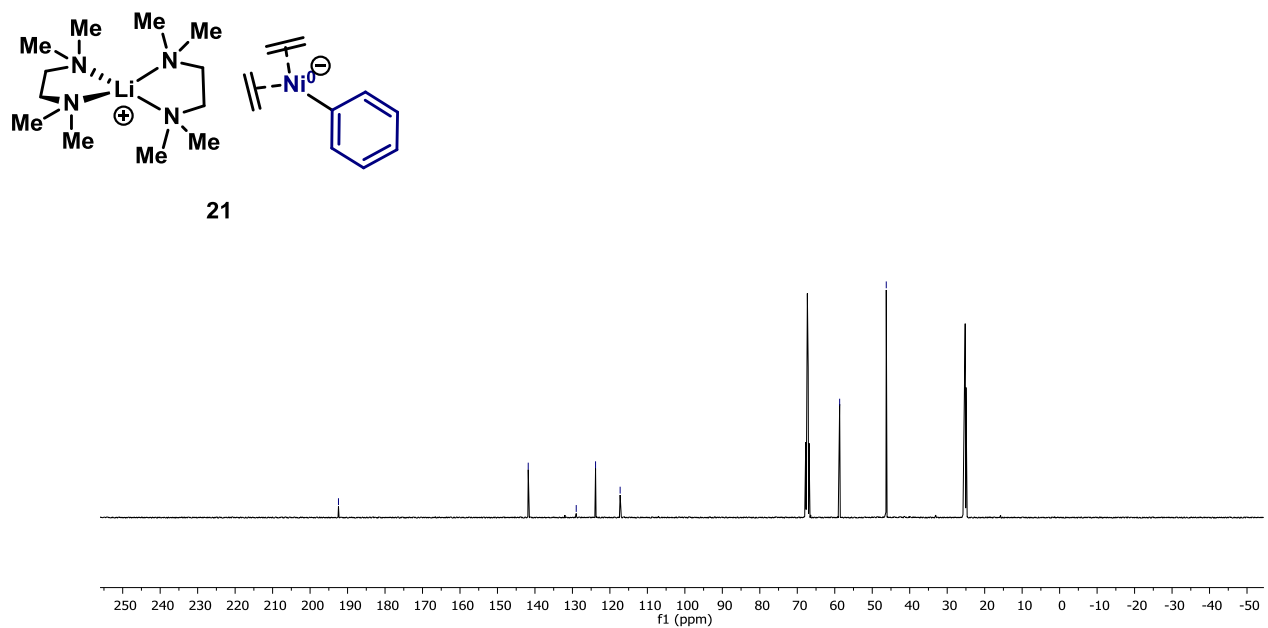




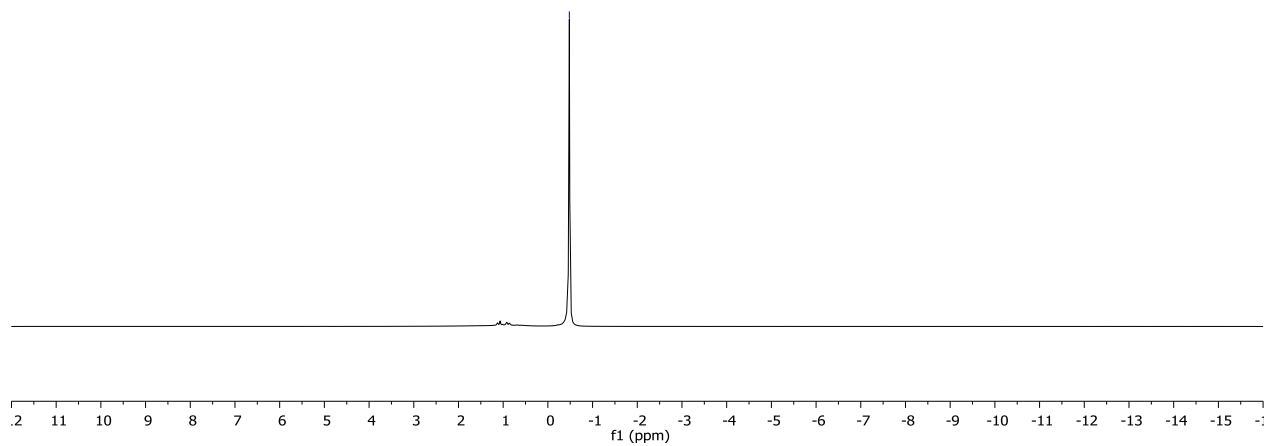
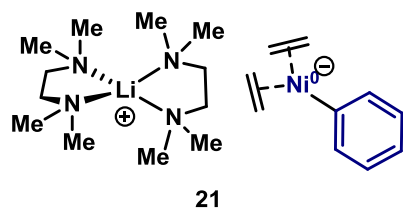
# <sup>1</sup>H NMR



# <sup>13</sup>C NMR



$^7\text{Li}$  NMR



## 14 References

1. Macchi, P.; Proserpio, D. M.; Sironi, A. *J. Am. Chem. Soc.* **1998**, *120*, 1447-1455.
2. In *Modern Organonickel Chemistry*, Tamaru. Y.; Ed., Wiley-VCH: Weinheim, 2005.
3. Buslov, I.; Song, F.; Hu, X. *Angew. Chem. Int. Ed.* **2016**, *55*, 12295-12299.
4. Müller, D.; Alexakis, A. *Org. Lett.* **2012**, *14*, 1842-1845.
5. Saranya, S.; Chand, S. S.; Gopalan, G.; Jijitha, V.; Radhakrishnan, K. V. *Synthesis* **2018**, *02*, 184-192.
6. Kuang, C.; Jiang, Y.; Yang, Q.; Zhang, W.; Wen, Y. *Zeitschrift für Naturforschung B*, **2008**, *63*, 865.
7. Qian, M.; Huang, Z.; Negishi, E. -i. *Org. Lett.* **2004**, *6*, 1531-1534.
8. He, Lu-Ying.; Schulz-Senft, M.; Tiedemann, B.; Linshoeft, J.; Gates, P.J.; Staubitz, A. *Eur. J. Org. Chem.* **2015**, *2015*, 2498-2502.
9. Leveque, C.; Chenneberg, L.; Corce, V.; Ollivier, C.; Fensterbank, L. *Chem. Commun.* **2016**, *52*, 9877-9880.
10. Tessier, P. E.; Nguyen, N.; Clay, M. D.; Fallis, A. G. *Org. Lett.* **2005**, *7*, 767-770.
11. Cahiez, G.; Gager, O.; Lecomte, F. *Org. Lett.* **2008**, *10*, 5255-5256.
12. Shen, R.; Chen, T.; Zhao, Y.; Qiu, R.; Zhou, Y.; Yin, S.; Wang, X.; Goto, M.; Han, L.-B. *J. Am. Chem. Soc.* **2011**, *133*, 17037-17044.
13. Zeng, H.; Hua, R. *J. Org. Chem.* **2008**, *73*, 558-562.
14. Nakao, Y.; Imanaka, H.; Sahoo, A. K.; Yada, A.; Hiyama, T. *J. Am. Chem. Soc.* **2005**, *127*, 6952-6953.
15. Lewis, J. C.; Bergman, R. G.; Ellman, J. A. *J. Am. Chem. Soc.* **2007**, *129*, 5332-5333.
16. Jang, Y. -J.; Yan, M. -C.; Lin, Y. -F.; Yao, C. -F. *J. Org. Chem.* **2004**, *69*, 3961-3963.